

## MINERALOGICAL NOTES

HOLLINGWORTHITE, A NEW RHODIUM MINERAL, IDENTIFIED  
BY ELECTRON PROBE MICROANALYSISE. F. STUMPFEL AND A. M. CLARK, *University College, London, England*

A number of recent publications (Genkin, 1959; Stumpfl, 1961; Genkin and Zvyagintsev, 1962; Genkin *et al.*, 1963) has shown that the mineralogy of the platinum group metals is much more complex than hitherto assumed. During the past decade, more than 20 new minerals of the platinum group metals have been described from deposits in the Soviet Union, South Africa and Canada. These discoveries have been of more than general mineralogical interest, and they have provided valuable new information on the processes involved in the formation of Pt deposits.

The considerable progress achieved in this field would not have been possible without the development of electron probe microanalysis. Most of the new minerals, even if present in considerable quantities in the respective ores, occur in extremely fine intergrowths with each other as well as with native platinum and sperrylite. Platinum concentrates from the Driekop mine, Transvaal, South Africa, have already yielded nine new platinum minerals (Stumpfl, 1961). Further microscopic investigation of this material has since proved the presence of fine grains of a medium grey, hard mineral. Its optical properties do not fit the data available on any of the other known platinum minerals. This mineral occurs as small grains (maximum diameter about 40 microns) closely intergrown with Rh-rich sperrylite, Rh-free sperrylite and geversite (Fig. 1). Its hardness is higher than that of sperrylite, its reflectivity distinctly lower. Comparative qualitative optical data are given in Table 1.

The respective grains are too small to perform quantitative measurements of reflectivity and microhardness with the methods available at present. The authors intend, however, to obtain these quantitative data using more advanced equipment in due course. *X*-ray microanalysis obviously was the only method suitable to obtain data on the composition of this phase. A *Cameca* "Microsonde" was used for the investigations. First, a qualitative survey of the distribution of elements in one of the areas in question was obtained by *x*-ray scanning images (Figs. 1, 2). The data obtained by quantitative *x*-ray microanalysis were corrected for absorption and atomic number effect following the method suggested by Thomas (1964) and for fluorescence (Birks, 1963). The results are tabulated in Table 2.

With the exception of sulfur, measured intensities are relative to pure element standards. The sulfur content of the two phases was determined

TABLE 1. COMPARATIVE QUALITATIVE OPTICAL DATA

Mineral	Reflectivity	Color Oil Immersion	Hardness
Native Pt.	70% <sup>1</sup> (relative to pyrite standard of 54.5%)	white	soft (126 Vickers Hardness <sup>1</sup> )
Geversite PtSb <sub>2</sub>	Very high but lower than Pt. (~65%)	white-grayish	>Pt.
Sperrylite	56% <sup>2</sup>	light-gray, brownish tint	>PtSb <sub>2</sub>
Rh-Sperrylite	40-45%	medium gray, bluish tint	>PtAs <sub>2</sub>
Hollingworthite	slightly lower than Rh-sperrylite	medium gray, slightly more pronounced bluish tint	>PtAs <sub>2</sub>

<sup>1</sup> Bowie and Taylor, 1958.<sup>2</sup> Ramdohr, 1960 (for "green" light).

TABLE 2. RESULTS OF QUANTITATIVE ELECTRON PROBE MICROANALYSIS

X-Ray-Line	Probe Energy keV	I <sub>A</sub> /I(A)%	True Concentration C <sub>A</sub> w <sup>0</sup>
<i>Hollingworthite</i>			
Pt L $\alpha$	34	9.84	10.3
Ir L $\alpha$	34	3.00	3.1
Rh L $\alpha$	19	23.66	30.8
Pd L $\alpha$	19	6.68	8.7
As K $\alpha$	34	32.23	32.6
S K $\alpha$	19	7.63	13.9
		83.04	99.4
<i>Rhodium Sperrylite</i>			
Pt L $\alpha$	34	22.53	23.8
Ir L $\alpha$	34	16.83	17.8
Rh L $\alpha$	19	8.86	11.6
Pd L $\alpha$	19	1.59	2.1
As K $\alpha$	34	30.84	30.7
S K $\alpha$	19	5.44	10.8
		86.09	96.8

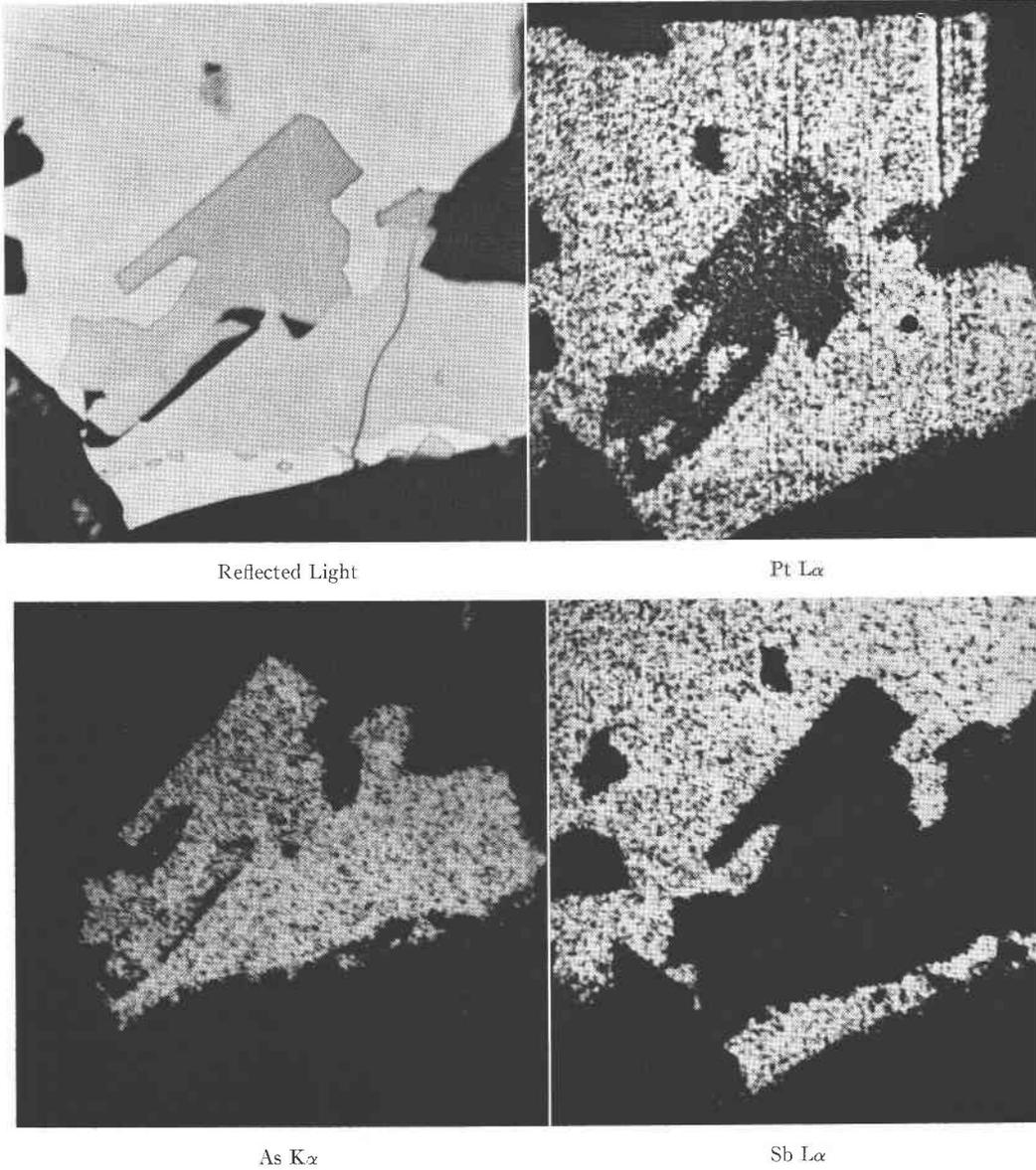


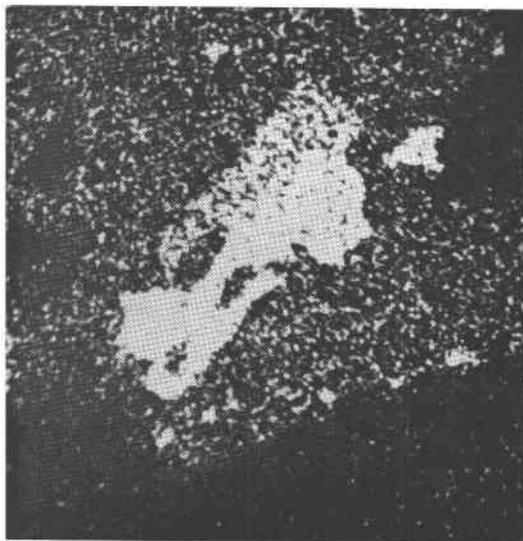
FIG. 1. Hollingworthite and Rh-rich Sperrylite (both medium gray), geversite (off-white) and sperrylite (light gray). Reflected light photomicrograph and scanning pictures in Pt, As and Sb radiation. Magnification  $\times 400$ .



Rh  $L\alpha$



Ir  $L\alpha$



Pd  $L\alpha$



S  $K\alpha$

FIG. 2 (Same minerals as in Fig. 1). Scanning pictures in Rh, Ir, Pd and S radiation. Magnification  $\times 400$ .

by comparing the emitted intensity with that from chalcopyrite ( $\text{CuFeS}_2$ ) which contains 34.9% S.

The measured intensities were corrected for effects due to absorption of the x-rays, atomic number differences and fluorescence. Considering the first two effects, the relation between emitted intensity and concentration is given by Thomas (1964) as:

$$\frac{I_A}{I(A)} = \frac{C_A^\alpha A A F(\chi) \text{ specimen}}{\sum_i C_i \alpha_i A F(\chi) \text{ std}}$$

$I_A$  is the intensity of emission of element A from the specimen as measured by the microanalyser.

$I(A)$  is the corresponding intensity from a pure sample of element A.

$C_A$  is the concentration of element A in the specimen. The subscripts i refer to the constituent elements of the matrix.

$F(\chi)$  is an absorption correction factor calculated from Philibert's relation (1962).

The  $\alpha$ -values were calculated as explained by Thomas (1964) from data by Brand (1936) and Nelms (1956, 1958). In order to simplify the calculation of corrections to six-element systems, the pairs of elements Platinum-Iridium and Rhodium-Palladium were considered together as they have adjacent atomic numbers, together with similar absorption coefficients and excitation energies. This effectively reduced the calculations from a six to a four-element system.

The fluorescence corrections were calculated by the method given by Birks (1963). Compared to the previous two factors this correction is, however, relatively insignificant, accounting for about 1.5% of the total composition.

The values given above for the Rh-rich phase correspond to the composition  $(\text{Rh}_{3.45}\text{Pd}_{0.94}\text{Pt}_{0.61}\text{Ir}_{0.19})_{5.19}\text{As}_{5.01}\text{S}_{4.99}$  or, simplified (Rh, Pt, Pd) (As, S)<sub>2</sub>. Optical data indicate that the mineral is cubic and the chemical composition corresponds generally to the  $\text{MAS}_2$ -type. This and the great similarity of the optical data to those of Rh-rich sperrylite (as discussed below) suggest that the new mineral has a pyrite type of structure (as sperrylite has:  $a = 5.94 \text{ \AA}$ ;  $Z = 4$ ).

The As:S ratio of 1:1 indicated that the new mineral might possibly be a member of the cobaltite group. This possibility has, however, been discarded because of two reasons:

1) cobaltite shows distinct anisotropy; the new mineral is isotropic. 2) Optical properties and microhardness of the new mineral are very similar to those of the closely associated rhodium sperrylite, which has an As:S ratio of 3:2.

The lattice of sperrylite is known to accommodate small amounts of Rh (Ramdohr, 1960). Considering the great similarity of the atomic radii (Pt=1.38 Å; Rh=1.34 Å) it seems possible that large amounts of Rh might replace Pt in a sperrylite-type structure without affecting the symmetry. A small portion of the metal positions is occupied by Pd (8.7%) and by Ir (3.1%). The considerable amount of mutual replacement possible amongst the platinum metals which may not affect the optical properties of the respective minerals has recently been stressed by one of us (Stumpfl, 1961). The comparatively high sulphur content (13.9%) is of interest. This kind of replacement of As by S in the lattice of sperrylite and related arsenides has not previously been noted. It may well be that intermediate members between Rh-rich sperrylite and the new mineral described in this note do exist. The name Hollingworthite is proposed for the new mineral, in honour of the eminent British geologist, Professor S. E. Hollingworth. This name should be used for all arsenides with a Rh:Pt ratio of  $> 1:1$ . It has been approved by the IMA Commission on New Minerals and Mineral Names.

Hollingworthite is closely associated with a Rh-rich sperrylite which contains 11.6% Rh and small amounts of Pd (2.1%) in addition to the main constituents. The results of quantitative electron probe microanalysis are tabulated in Table 2 ("Rhodium Sperrylite"). They correspond to the formula  $(\text{Pt}_{1.47}\text{Ir}_{1.12}\text{Rh}_{1.37}\text{Pd}_{0.23})_{4.19}\text{As}_{5.93}\text{S}_{4.07}$ . There is only a slight difference in reflectivity which is not easily noticed but the reflectivity seems to decrease with increasing Rh-content. Simultaneously the color tends to become more bluish-gray as the Rh-content increases. Some qualitative microscope observations are given in Table 1.

It is interesting to note that no rhodium minerals have so far been found in ores from the Merensky Reef in the Rustenburg mines, Transvaal (Millman and Kingston, oral comm.). The obvious difference in the ore mineralogy of the Merensky Reef and the dunite pipe Pt-deposits is further underlined by the fact that Kingston and Millman (oral comm.) have discovered a number of tellurides of the platinum metals in the Rustenburg deposits. Only very small amounts of tellurides have so far been detected in the concentrates from the Driekop pipe. Electron probe microanalysis shows that they correspond most probably to the phase (Pt, Bi) Te detected by Kingston and Millman (oral comm.) in Rustenburg ores.

Limited data only are available on synthetic Rh-compounds. The system Rh-As has so far not been investigated. Juza *et al.* (1935) have proved the existence of the phases  $\text{Rh}_9\text{S}_8$ ,  $\text{Rh}_3\text{S}_4$ ,  $\text{Rh}_2\text{S}_3$  and  $\text{Rh}_2\text{S}_5$ . One of the results of their investigations was the observation that the powder patterns of  $\text{Rh}_2\text{S}_5$  and  $\text{FeS}_2$  are similar. They did not, however, find any

evidence for  $\text{RhS}_2$ , which Thomassen (1929) had synthesized ( $\text{RhS}_2$  with  $a = 5.574 \pm 0.005 \text{ \AA}$ ). On the other hand, Geller and Cetlin (1955) have described a phase  $\text{RhSe}_2$ , with pyrite structure.

## ACKNOWLEDGMENTS

The authors would like to acknowledge the support of D.S.I.R. in equipping and financing this research. Thanks are due to Prof. S. E. Hollingworth for much encouragement and to Dr. M. Fleischer, Washington, for helpful and constructive criticism and for supplying translations of the Russian papers. Dr. R. W. R. Rutland kindly read the manuscript.

## REFERENCES

- BIRKS, L. S. (1963) *Electron-Probe Microanalysis*. Interscience Publ., New York/London.
- BOWIE, S. H. U. AND K. TAYLOR (1958) A system of ore mineral identification. *Mining Mag.* **96**, 265–277, 337–345.
- BRAND, J. O. (1936) Ueber die Energieverteilung rückdiffundierter Kathodenstrahlen. *Ann. Physik*, 5. Folge, **26**, 609–624.
- GELLER, S. AND B. B. CETLIN (1955) The crystal structure of  $\text{RhSe}_2$ . *Acta Cryst.* **8**, 272–274.
- GENKIN, A. D. (1959) Conditions of occurrence and features of the composition of minerals of the platinum group in ores of the Norilsk deposits. *Akad. Nauk SSSR, Geol. Rudn. Mestorozhdenii*, **6**, 74–84.
- AND O. E. ZVYAGINTSEV (1962) Vysotskite, a new sulphide of palladium and nickel. *Zapiski Vses. Mineral. Oshch.* **91**, (6), 718–725.
- N. N. ZHURAVLEV AND E. M. SMIRNOVA (1963) Moncheite and kotulskite—new minerals—and the composition of michenerite. *Zapiski Vses. Mineral. Obshch.* **92** (1), 33–50.
- JUZA, R., O. HUELSMANN AND K. MEISEL, (1935) Über die Sulfide des Rhodiums. *Zeit. anorg. Chem.* **225**, 369–385.
- NELMS, A. T. (1956) *U. S. Natl. Bur. Stand., Circ.* **577**.
- (1958) *U. S. Natl. Bur. Stand., Suppl. to Circ.* **577**,
- PHILIBERT, J. (1963) A method for calculating the absorption correction in electron-probe microanalysis. *X-ray Optics and X-ray Microanalysis* (H. H. Pattee, V. E. Cosslett, Arne Engström, editors). Academic Press, New York—London.
- RAMDOHR, P. (1960) *Die Erzminerale und ihre Verwachsungen*. Akademie-Verlag, Berlin
- STUMPFL, E. F. (1961) Some new platinoid-rich minerals, identified with the electron microanalyser. *Mineral. Mag.* **32**, 833–847.
- THOMAS, P. M. (1964) A method for correcting for atomic number effects in electron probe microanalysis. *U.K.A.E.R.E. Research Group Rept.* R **4593**.
- THOMASSEN, L. (1929) Über Kristallstrukturen einiger binärer Verbindungen der Platinmetalle. II. *Zeit. phys. Chem.* **4**, 283–287.