

## Rhodarsenide, (Rh,Pd)<sub>2</sub>As, a new mineral

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**Abstract:** The new mineral rhodarsenide, ideally (Rh, Pd)<sub>2</sub>As, has been found in concentrates from placers of the Srebrnica river, near the village Veluce in Central Serbia. The associated platinum-group minerals are PGE alloys, Rh-Ir sulpharsenides and sperrylite. Rhodarsenide is present as inclusions (up to 80 × 100 μm) in Pt-Fe and Ru-Os-Ir alloys. In reflected light it is brownish; pleochroism and anisotropy are weak to distinct. Maximum and minimum reflectance values in air for standard wavelengths (470, 546, 589 and 650 nm) are 46.3/45.5, 48.4/47.6, 49.5/48.2 and 51.2/49.8, respectively; values measured in oil are 38.2/32.9 (470), 39.8/35.7 (546), 40.4/36.4 (589) and 40.5/36.6 (650). Vickers micro-indentation hardness (VHN<sub>25</sub>) is 493-585 kg/mm<sup>2</sup>. Chemical compositions of individual grains of rhodarsenide vary between Rh 38.53-60.81, Pd 12.10-34.67, Pt 0.00-2.38, Ir 0.09-0.48, Fe 0.00-0.10, Cu 0.08-0.46, As 23.42-27.96, Sb 0.09-1.60, and Te 0.08-1.20 wt.%, corresponding to: (Rh<sub>1.67</sub>Pd<sub>0.34</sub>)Σ<sub>2.01</sub>As<sub>0.99</sub> and (Rh<sub>1.07</sub>Pd<sub>0.94</sub>Pt<sub>0.03</sub>)Σ<sub>2.04</sub>(As<sub>0.91</sub>Sb<sub>0.04</sub>Te<sub>0.01</sub>)Σ<sub>0.96</sub>. The X-ray powder-diffraction pattern was indexed for an orthorhombic cell with  $a = 5.866 \text{ \AA}$ ;  $b = 3.893 \text{ \AA}$ ;  $c = 7.302 \text{ \AA}$ ;  $a : b : c = 1.507 : 1 : 1.875$ ;  $V = 166.7 \text{ \AA}^3$ . For  $Z = 4$ , the calculated density is 11.32 g/cm<sup>3</sup>. The three strongest lines in the X-ray pattern are 2.237 (10), 2.067 (8) and 2.426 (7) Å.

**Key-words:** rhodarsenide, new mineral, PGM placers, Central Serbia.

### Introduction

Rhodarsenide, ideally (Rh,Pd)<sub>2</sub>As, is a new platinum-group mineral (PGM) discovered in PGM-bearing placers of the Srebrnica river, near Veluce, in Central Serbia. The mineralogy of the placers has recently been described by Krstić & Tarkian (1997). They contain a wide variety of PGM consisting of PGE alloys, sulphides, arsenides, sulpharsenides, tellurides, and antimonides. The PGM associated with rhodarsenide are Pt-Fe alloys, Ru-Os-Ir alloys, hollingworthite,

irarsite, and sperrylite. The source rocks of the placers are chromitites of the Veluce ophiolite complex, in which most of the PGM precipitated from a silicate melt under magmatic conditions (Krstić & Tarkian, 1997).

The new mineral and its name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association (No. 96-030). The mineral name is for the composition (Rh > Pd)<sub>2</sub>As. Type material is deposited in the Mineralogical Museum of the University of Hamburg.

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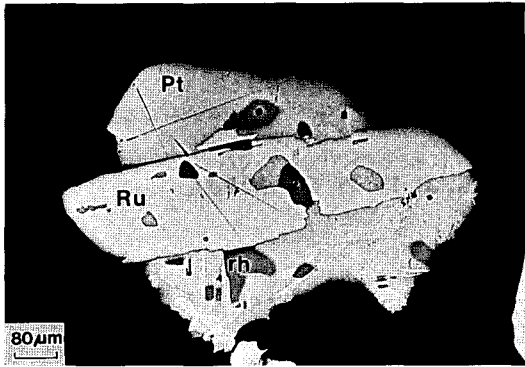


Fig. 1. Photomicrograph of rhodarsenide inclusions (rh) in Pt-Fe-alloy (Pt) and Ru-Os-Ir alloy (Ru). Reflected light.

### Physical and optical properties

Rhodarsenide occurs as irregular inclusions in Pt-Fe- and Ru-Os-Ir alloys. The size of individual grains varies between  $10 \times 70$  and  $80 \times 100 \mu\text{m}$  (Fig. 1). Vickers microhardness VHN (25 g load) is on average 515 (6 indentations), and the range is 493-585  $\text{kg}/\text{mm}^2$ . Accordingly, it is harder than palladoarsenide  $\text{Pd}_2\text{As}$  ( $\text{VHN}_{20} = 277\text{-}357$ , Begizov *et al.*, 1974) and palladobismutharsenide,  $\text{Pd}_{10}\text{As}_4\text{Bi}$  ( $\text{VHN}_{25} = 373\text{-}483$ , Cabri *et al.*, 1976), but softer than cherepanovite, RhAs ( $\text{VHN}_{50} = 726\text{-}754$ , Rudashevsky *et al.*, 1985).

In reflected light, rhodarsenide is brownish with a pale-green tinge. Pleochroism is weak in

Table 1. Reflectance data of rhodarsenide.

| $\lambda\text{nm}$             | $R_1$ (air) | $R_2$ (air) | $R_1$ (oil) | $R_2$ (oil) |
|--------------------------------|-------------|-------------|-------------|-------------|
| 400                            | 41.8        | 39.4        | 35.2        | 30.5        |
| 420                            | 43.2        | 41.1        | 35.7        | 31.1        |
| 440                            | 44.5        | 42.8        | 36.6        | 31.7        |
| 460                            | 45.9        | 44.5        | 37.9        | 32.5        |
| 470                            | 46.3        | 45.5        | 38.2        | 32.9        |
| 480                            | 47.2        | 46.2        | 38.7        | 33.9        |
| 500                            | 48.6        | 47.9        | 39.3        | 34.5        |
| 520                            | 49.2        | 48.1        | 39.3        | 35.1        |
| 540                            | 49.9        | 48.4        | 39.8        | 35.6        |
| 546                            | 48.4        | 47.6        | 39.8        | 35.7        |
| 560                            | 49.7        | 48.3        | 40.1        | 36.1        |
| 580                            | 49.5        | 48.3        | 40.4        | 36.5        |
| 589                            | 49.5        | 48.2        | 40.4        | 36.4        |
| 600                            | 50.2        | 49.3        | 40.5        | 36.4        |
| 620                            | 51.0        | 50.3        | 40.7        | 36.6        |
| 640                            | 51.0        | 50.2        | 40.5        | 36.5        |
| 650                            | 51.2        | 49.8        | 40.5        | 36.6        |
| 660                            | 51.0        | 50.0        | 40.5        | 36.8        |
| 680                            | 52.0        | 50.8        | 40.6        | 36.8        |
| 700                            | 53.2        | 51.6        | 40.5        | 36.6        |
| Colour values ( C illuminant ) |             |             |             |             |
|                                | x           | y           | Y%          | Pe%         |
| $R_1$ (air)                    | 0.318       | 0.327       | 49.6        | 5.1         |
| $R_2$ (air)                    | 0.319       | 0.328       | 48.4        | 5.7         |
| $R_1$ (oil)                    | 0.317       | 0.325       | 39.9        | 4.0         |
| $R_2$ (oil)                    | 0.320       | 0.329       | 35.8        | 5.9         |

air but distinct (from brownish to greenish) in oil immersion. The anisotropism is moderate to distinct, from dark brown to greenish grey.

A computerized Zeiss MPM microphotometer and a WTiC standard ( $R_{589}$  in air = 49.5 %,  $R_{589}$  in oil = 35.5 %) were used for reflectance measurements (Table 1 and Fig. 2). The reflectance

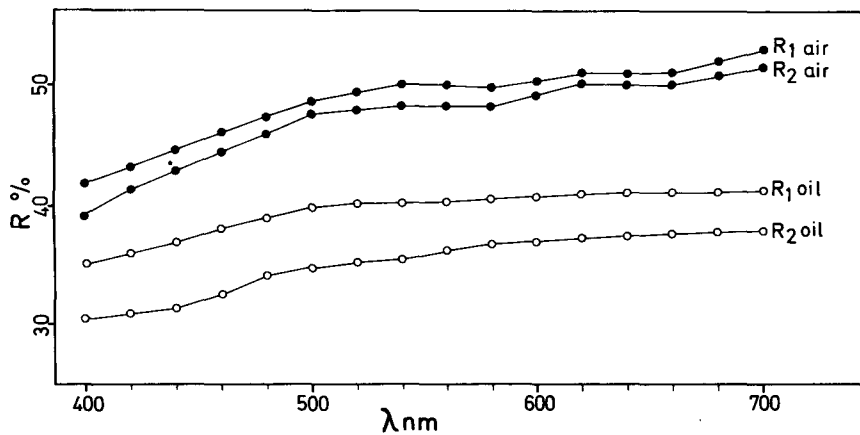


Fig. 2. Reflectance spectra for rhodarsenide in air and oil.

Table 2. Representative electron-microprobe analyses of rhodarsenide (wt.%).

| No.                             | 1      | 2      | 3      | 4     | 5     | 6      |
|---------------------------------|--------|--------|--------|-------|-------|--------|
| Rh                              | 60.81  | 57.63  | 57.18  | 42.01 | 40.34 | 38.53  |
| Pd                              | 12.65  | 15.74  | 12.10  | 29.88 | 30.70 | 34.67  |
| Pt                              | 0.49   | 1.78   | 2.38   | -     | 1.95  | 1.90   |
| Ir                              | -      | 0.20   | -      | -     | 0.09  | 0.48   |
| Fe                              | -      | -      | -      | -     | -     | 0.10   |
| Cu                              | 0.08   | -      | 0.19   | -     | 0.46  | -      |
| As                              | 26.04  | 24.00  | 27.96  | 25.74 | 23.37 | 23.42  |
| Sb                              | 0.09   | 0.67   | 0.15   | 1.60  | 1.08  | 1.55   |
| Te                              | -      | -      | 0.08   | -     | 1.20  | 0.50   |
| Total                           | 100.16 | 100.02 | 100.04 | 99.23 | 99.19 | 101.15 |
| Atomic proportions (Σatoms = 3) |        |        |        |       |       |        |
| Rh                              | 1.67   | 1.60   | 1.57   | 1.17  | 1.14  | 1.07   |
| Pd                              | 0.34   | 0.42   | 0.32   | 0.81  | 0.84  | 0.94   |
| Pt                              | -      | 0.03   | 0.04   | -     | 0.03  | 0.03   |
| Ir                              | -      | -      | -      | -     | -     | -      |
| Fe                              | -      | -      | -      | -     | -     | -      |
| Cu                              | -      | -      | 0.01   | -     | 0.02  | -      |
| Σ Me                            | 2.01   | 2.05   | 1.94   | 1.98  | 2.03  | 2.04   |
| As                              | 0.99   | 0.93   | 1.06   | 0.98  | 0.91  | 0.91   |
| Sb                              | -      | 0.02   | -      | 0.04  | 0.03  | 0.04   |
| Te                              | -      | -      | -      | -     | 0.03  | 0.01   |
| Σ                               | 0.99   | 0.95   | 1.06   | 1.02  | 0.97  | 0.96   |
| Rh/Rh+Pd                        | 0.83   | 0.79   | 0.83   | 0.59  | 0.57  | 0.53   |

curves of rhodarsenide resemble those of palladoarsenide (Begizov *et al.*, 1974) and cherepanovite (Rudashevsky *et al.*, 1985). However, the reflectance values of rhodarsenide (average at 589 nm = 49 %) lie between those reported for palladoarsenide (53 %) and cherepanovite (46 %). Reflectance spectra for palladobismutharsenide appear to be different, though data given by Cabri *et al.* (1976) are for the four standard wavelengths ( $R_{589}$ : ≈ 54 %) only.

### Chemical composition

Several grains of rhodarsenide were analyzed using a Cameca Camebax Microbeam wavelength-dispersive electron microprobe at the Department of Mineralogy and Petrology, University of Hamburg. The operating conditions were 20 kV and 20 nA. The following X-ray lines were used: RhL $\alpha$ , PdL $\beta$ , PtL $\alpha$ , IrL $\alpha$ , FeK $\alpha$ , CuK $\alpha$ , AsK $\alpha$ , SbL $\alpha$ , TeL $\alpha$ . Pure elements (Rh, Pt, Ir, Fe, Cu) as well as synthetic PdBiTe, GaAs, and Sb<sub>2</sub>S<sub>3</sub> were used as standards. Corrections were applied using the computer program "PAP" (Pouchou & Pichoir, 1991).

Representative analyses of rhodarsenide are given in Table 2. Platinum is present as a minor

element (up to 3 wt. %) in most analyses. Ir was detected in some analyses, however, in amounts less than 0.5 wt. %. Arsenic is partly replaced by Sb (up to 3 wt. %) and Te (up to 1.5 wt. %). The composition is close to stoichiometric Me<sub>2</sub>As, with variation of Rh/Rh+Pd from 0.83 to 0.53. Accordingly the ideal formula is (Rh,Pd)<sub>2</sub>As for the mineral. The only PGM comparable with this composition is an unnamed mineral with the formula (Rh,Pd)<sub>5-x</sub>(As,Te)<sub>2</sub> or ideally Rh<sub>5</sub>Pd<sub>5</sub>As<sub>4</sub> (without additional data) described by Johan *et al.* (1991) in isoferroplatinum nuggets from Milverton, Australia. However, the chemical formula of this mineral reported by Johan *et al.*, (1991) shows considerable deviation from the 2:1 stoichiometry.

Analyses of palladoarsenides from the type locality (Begizov *et al.*, 1974), the Stillwater complex (Cabri *et al.*, 1975; Volborth *et al.*, 1986) and from Lac des Iles, Ontario (Cabri & Laflamme, 1979) do not show any Rh. In addition, palladobismutharsenide (Cabri *et al.*, 1976) is devoid of Rh. However, significant variation of Rh/Rh+Pd ratios in rhodarsenide implies an extensive solid-solution between Pd<sub>2</sub>As (palladoarsenide) and Rh<sub>2</sub>As, whereas the latter was known as a synthetic phase only (Quesnel & Heyding, 1962).

Table 3. Comparison of X-ray data of rhodarsenide and synthetic  $\beta$ -Rh<sub>2</sub>As.

| Rhodarsenide      |                    |                    |         | Synthetic $\beta$ -Rh <sub>2</sub> As<br>(Quesnel & Heyding, 1962) |       |     |
|-------------------|--------------------|--------------------|---------|--|-------|-----|
| $I_{\text{est.}}$ | $d_{\text{meas.}}$ | $d_{\text{calc.}}$ | hkl     | I  | d     | hkl |
| 7                 | 2.426              | 2.425              | 112     | 80   | 2.424 | 112 |
| 4                 | 2.348              | 2.343              | 210     | 40   | 2.343 | 210 |
|                   |                    |                    |         | 20   | 2.289 | 202 |
|                   |                    |                    |         | 20   | 2.248 | 103 |
| 10                | 2.237              | 2.231              | 211     | 100  | 2.232 | 211 |
| 8                 | 2.067              | 2.064              | 013     | 40   | 2.071 | 013 |
| 6                 | 1.935              | 1.945              | 020,113 | 80   | 1.947 | 020 |
|                   |                    |                    |         | 20   | 1.894 | 301 |
| 5                 | 1.860              | 1.873              | 203     | 20   | 1.878 | 203 |
| 3                 | 1.828              | 1.825              | 004     | 18   | 1.832 | 004 |
|                   |                    |                    |         | 6  | 1.751 | 104 |
|                   |                    |                    |         | 20   | 1.731 | 302 |
| 1                 | 1.694              | 1.699              | 311     | 14   | 1.703 | 311 |
|                   |                    | 1.688              | 213     | 18   | 1.692 | 213 |
| 1                 | 1.610              | 1.622              | 220     |  |       |     |
|                   |                    |                    |         | 6  | 1.598 | 114 |
| 2                 | 1.548              | 1.550              | 204     |  |       |     |
|                   |                    |                    |         | 14   | 1.487 | 222 |
| 1                 | 1.475              | 1.472              | 123     | 20   | 1.475 | 123 |
|                   |                    |                    |         | 14   | 1.445 | 401 |
| 1                 | 1.426              | 1.419              | 313     | 14   | 1.423 | 313 |
|                   |                    | 1.417              | 105     |  |       |     |
| 3                 | 1.384              | 1.379              | 320     |  |       |     |
|                   |                    |                    |         | 14   | 1.374 | 410 |
| 1                 | 1.351              | 1.355              | 321     | 25   | 1.358 | 321 |
| 1                 | 1.337              | 1.334              | 304     | 14   | 1.337 | 304 |
|                   |                    | 1.331              | 115,024 |  |       |     |
| 3                 | 1.306              | 1.307              | 205     | 14   | 1.314 | 205 |
| 1                 | 1.300              | 1.298              | 124     |  |       |     |
| 1                 | 1.291              | 1.290              | 322     | 35   | 1.296 | 322 |
| 2                 | 1.278              | 1.278              | 031     |  |       |     |
| 1                 | 1.268              | 1.267              | 314     | 35   | 1.268 | 314 |
| 1                 | 1.258              | 1.256              | 403     |  |       |     |
|                   |                    |                    |         | 8  | 1.247 | 131 |
| 1                 | 1.218              | 1.217              | 006     |  |       |     |
| 1                 | 1.212              | 1.212              | 224     | 6  | 1.216 | 224 |
|                   |                    |                    |         | 18   | 1.201 | 323 |

### X-ray data

Single-crystal studies of rhodarsenide could not be performed on the material available. Thus, three crystals analysed by electron microprobe were studied using a Rigaku microdiffractometer ( $\text{CrK}\alpha$ ). The X-ray pattern obtained is presented in Table 3. With the exception of some reflections the data are different from those of palladoarsenide (monoclinic) (Begizov *et al.*, 1974) and of synthetic Pd<sub>2</sub>As (Saini *et al.*, 1964; Bälz & Schubert, 1969). The latter has been reported as monoclinic ( $\alpha$ -form), hexagonal ( $\beta$ -form) and orthorhombic phases. The X-ray data of rhodar-

senide show more similarity to those reported for the synthetic equivalent of palladobismutharsenide (Cabri *et al.*, 1976), although only the strongest line (2.237) coincides.

The X-ray pattern of rhodarsenide is, however, in good agreement with that obtained for synthetic  $\beta$ -Rh<sub>2</sub>As (orthorhombic,  $a = 5.89$ ;  $b = 3.89$ ;  $c = 7.32$  Å) by Quesnel & Heyding (1962, Table 3). Thus the pattern was indexed for an orthorhombic cell by analogy with that of synthetic  $\beta$ -Rh<sub>2</sub>As. Refinement of the data yielded for rhodarsenide:  $a = 5.866(5)$  Å;  $b = 3.893(2)$  Å;  $c = 7.302(4)$  Å;  $a : b : c = 1.507 : 1 : 1.875$ ;  $V = 166.7$  Å<sup>3</sup>. For  $Z = 4$ , the density calculated

for a composition (Table 2, analysis No. 4) is 11.32 g/cm<sup>3</sup>.

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### References

- Bälz, U. & Schubert, K. (1969): Kristallstruktur von Pd<sub>2</sub>As(r) und Pd<sub>2</sub>Sb. *Less-Common Metals*, **19**, 300-304.
- Begizov, V.C., Meshchankina, V.I., Dubakina, L.S. (1974): Palladoarsenide, Pd<sub>2</sub>As, a new natural palladium arsenide from the copper-nickel ores of the Oktyabr deposits. *Zap.Vses. Mineral. Obshchest.*, **103**, 104-107 (in Russian) (Translation in *Internat. Geol.Rev.*, **16**, 1294-1297).
- Cabri, L.J. & Laflamme, J.H.G. (1979): Mineralogy of samples from the Lac des Iles area, Ontario. *CAN-MET Report*, Dept. Energy, Mines and Resources, Ottawa, 17-21.
- Cabri, L.J., Stewart, J.M., Rowland, J.F., Chen, T.T. (1975): New data on some palladium arsenides and antimonides. *Can. Mineral.*, **13**, 321-335.
- Cabri, L.J., Chen, T.T., Stewart, J.M., Laflamme, J.H.G. (1976): Two new palladium-arsenic-bismuth minerals from the Stillwater complex, Montana. *Can. Mineral.*, **14**, 410-413.
- Johan, Z., Slansky, E., Ohnenstetter, M. (1991): Isoferroplatinum nuggets from Milverton (Fifield, N.S.W., Australia): a contribution to the origin of PGE mineralization in Alaska-type complexes. *C.R. Acad. Sci. Paris*, **312**, Ser II, 55-60.
- Krstić, S. & Tarkian, M. (1997): Platinum-group minerals in gold-bearing placers associated with the Veluce ophiolite complex, Yugoslavia. *Can. Mineral.*, **35**, 1-21.
- Pouchou, J.L. & Pichoir, F. (1991): Quantitative analysis of homogeneous or stratified microvolumes applying the model "PAP". in: "Electron Probe Quantitation", K.F.J. Heinrich & D.E. Newbury, eds. Plenum Press, New York, 31-75.
- Quesnel, J.C. & Heyding, R.D. (1962): Transition metal arsenides. A note on the rhodium/arsenic system and the monoclinic diarsenides of the cobalt family. *Can. J. Chem.*, **40**, 814-818.
- Rudashevsky, N.S., Mochalov, A.G., Trubkin, N.V., Shumskaya, N.I., Shkurski, V.I., Evstigneeva, T.L. (1985): Cherepanovite RhAs - a new mineral. *Zapiski Vses Mineral Obshch.*, **114**, 464-469 (in Russian).
- Saini, G.S., Calvert, L.D., Heyding, R.D., Taylor, J.B. (1964): Arsenides of the transition metals. VII. The palladium-arsenic system. *Can. J. Chem.*, **42**, 620-629.
- Volborth, A., Tarkian, M., Stumpfl, E.F., Housley, R.M. (1986): A survey of the Pd-Pt mineralization along the 35-km strike of the J-M Reef, Stillwater complex, Montana. *Can. Mineral.*, **24**, 329-346.

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