

Rhodarsenide, (Rh,Pd)₂As, a new mineral

MAHMUD TARKIAN^{1,*}), SAŠA KRSTIĆ²), KARL-HEINZ KLASKA¹)
and WILFRIED LIEBMAN¹)

¹) Institute of Mineralogy and Petrology, University of Hamburg,
Grindelallee 48, D-20146 Hamburg, Germany

²) Department of Geology, Earth Science Centre, University of Toronto,
22 Russell Street, Toronto, Ontario, Canada M5S 3B1

Abstract: The new mineral rhodarsenide, ideally (Rh, Pd)₂As, 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 (VHN₂₅) is 493-585 kg/mm². 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_{1.67}Pd_{0.34})Σ_{2.01}As_{0.99} and (Rh_{1.07}Pd_{0.94}Pt_{0.03})Σ_{2.04}(As_{0.91}Sb_{0.04}Te_{0.01})Σ_{0.96}. 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/cm³. 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)₂As, 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)₂As. Type material is deposited in the Mineralogical Museum of the University of Hamburg.

* e-mail: mi6a005@mineralogie.uni-hamburg.de

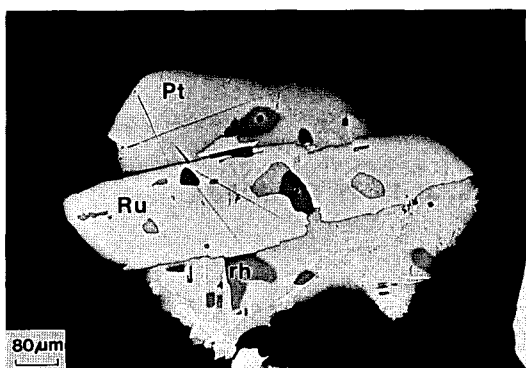


Fig. 1. Photomicrograph of rhodarsenide inclusions (rh) in Pt-Fe-alloy (Pt) and Ru-Os-Ir alloy (Ru). Reflected light.

Physical and optical properties

Rhodarsenide occurs as irregular inclusions in Pt-Fe- and Ru-Os-Ir alloys. The size of individual grains varies between 10×70 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 kg/mm^2 . Accordingly, it is harder than palladoarsenide Pd_2As ($\text{VHN}_{20} = 277\text{-}357$, 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.

λnm	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

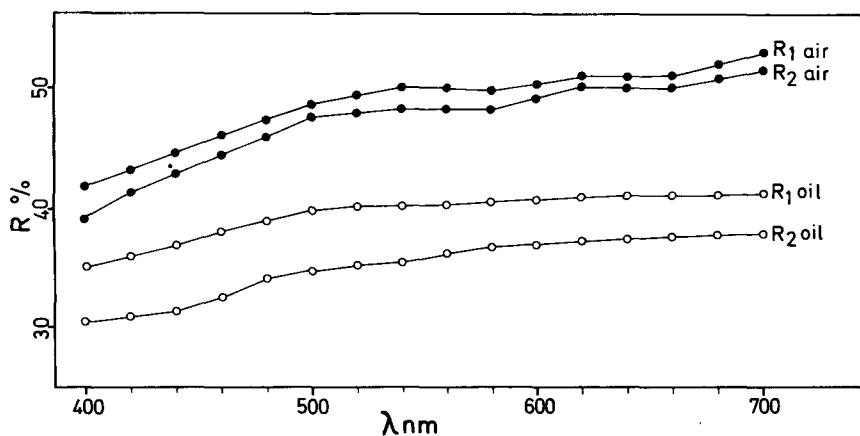


Fig. 2. Reflectance spectra for rhodarsenide in air and oil.

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 α , PdL β , PtL α , IrL α , FeK α , CuK α , AsK α , SbL α , TeL α . Pure elements (Rh, Pt, Ir, Fe, Cu) as well as synthetic PdBiTe, GaAs, and Sb₂S₃ 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 Me₂As, with variation of Rh/Rh+Pd from 0.83 to 0.53. Accordingly the ideal formula is (Rh,Pd)₂As for the mineral. The only PGM comparable with this composition is an unnamed mineral with the formula (Rh,Pd)_{5-x}(As,Te)₂ or ideally Rh₅Pd₅As₄ (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 Pd₂As (palladoarsenide) and Rh₂As, whereas the latter was known as a synthetic phase only (Quesnel & Heyding, 1962).

Table 3. Comparison of X-ray data of rhodarsenide and synthetic β -Rh₂As.

Rhodarsenide				Synthetic β -Rh ₂ As (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 Pd₂As (Saini *et al.*, 1964; Bälz & Schubert, 1969). The latter has been reported as monoclinic (α -form), hexagonal (β -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 β -Rh₂As (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 β -Rh₂As. Refinement of the data yielded for rhodarsenide: $a = 5.866(5)$ Å; $b = 3.893(2)$ Å; $c = 7.302(4)$ Å; $a : b : c = 1.507 : 1 : 1.875$; $V = 166.7$ Å³. For $Z = 4$, the density calculated

for a composition (Table 2, analysis No. 4) is 11.32 g/cm³.

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