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RHODIUM, PLATINUM, AND GOLD ALLOYS FROM THE STILLWATER COMPLEX*

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Abstract

Four platinum-group native alloys from the Stillwater Complex, Montana, are characterized. Platinian rhodium is a newly discovered mineral with composition $Rh_{.57}Pt_{.43}$; it is cubic with $a =$ 3.856(1)Å. Rhodian platinum, also newly discovered, has a composition $\sim Pt_{.68}Rh_{.32}$ with $a =$ 3.886(1)Å. Platinum-iron alloy with a composition close to Pt_3Fe is in contrast to iron-free platinum which contains minor Pd and Ir. Palladian gold (Au,Pd) with $a = 4.047(1)$Å, has also been found and characterized.

Introduction

Rock samples and heavy mineral concentrates from the Banded and Upper zones of the Stillwater Complex, Montana, which consist of norites, gabbros and anorthosites, were studied to determine the mineralogical nature of the platinum-group elements. This paper reports the newly identified mineral species rhodium and some other native alloys among the numerous and often complex platinum-group minerals (PG-minerals) which have been identified so far.

Geology and Previous Work

The stratiform Precambrian Stillwater Complex, on the northern margin of the Beartooth Mountains, southwestern Montana, has been characterized into several major units or zones by Hess (1960), Jones *et al.* (1960), Jackson (1961, 1963) and Page & Nokleberg (1970). Much careful mineralogical work on the opaque minerals of the Basal zone and the chromitite layers has been reported by Page & Jackson (1967), Leonard *et al.* (1969), Page (1971), and Page *et al.* (1972). Page *et al.* (1973) have summarized the PG-minerals identified from the Stillwater Complex, to that date, as stibiopalladinite, sperrylite, cooperite, platinum-iron alloy, and laurite. The stibiopalladinite from the Upper zone had been identified only by optical and etch methods (Howland *et al.* 1936). The PG-minerals were usually found as inclusions (average diameter 5-10 μm) in chromite and in interstitial sulphides. Preliminary data for two unidentified PG-minerals were also earlier reported by Page & Jackson (1967) but further work showed that these were 4- and 5-micron diameter grains with Os and Ir as principal constituents (Page, written comm. 20/12/72). A complex intergrowth of merenskyite and kotulskite was recently reported by Cabri & Pickwick (1974).

Materials and Method of Investigation

The PG-minerals characterized in this work came from two sampling points, approximately 1500 feet apart, in the Banded and Upper zones. Sample JGWT-3 was received as a heavy mineral concentrate whereas Sample 789-T-1-1 was received both as a heavy mineral concentrate and as rock hand-specimens. The rock sample was crushed and the PG-minerals were concentrated by making gravity separations of sized fractions with separatory funnels (2.96 liquid) and with an elutriating tube (3.33 liquid). All the samples were mounted in cold-setting plastic, polished on lead laps, and lightly buffed on a cloth lap using minus 0.05-μm alumina. Reflectance values were obtained with reference to a silicon standard, N 2538.42, calibrated by the National Physical Laboratory, United Kingdom, using a 16.5:1 objective of 0.40 numerical aperture. The micro-indentation hardness measurements were made with a Leitz Durimet tester. *X*-ray diffraction powder data were obtained by the film method using 57.3 and 114.6 mm Gandolfi cameras. Film shrinkage corrections were applied and the unit-cell parameters were refined by a least-squares computer program PARAM (Stewart *et al.* 1972).

The compositions were determined using a Materials Analysis Company Model 400 electron probe microanalyser, operated at 25 kv and with a specimen current of about 0.03 mi-

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croamperes. The following x-ray lines and synthetic standards were used: Sb$L\alpha$, (PdSb); Pd$L\alpha$, Bi$L\alpha$, Te$L\alpha$ (PdBiTe); Cu$K\alpha$, Au$L\alpha$, Pd$L\alpha$, Ir$L\alpha$, Ni$K\alpha$ (pure metals); Pt$L\alpha$, Rh$L\alpha$ ($Pt_{.8}Rh_{.2}$); Au$L\alpha$, Ag$L\alpha$ ($Au_{.8}Ag_{.2}$) and Pt$L\alpha$ Fe$K\alpha$ (Pt_3Fe). Corrections to these x-ray data were applied both with the EMPADR VII computer program of Rucklidge & Gasparrini (1969) and the MAGIC IV computer program by J. W. Colby, Bell Telephone Laboratories, Inc., Allentown, Pa.

Optical, Physical and Chemical Properties of the PG-Minerals

The PG-minerals found in our studies so far consist of: a) the native alloys — platinian rhodium, rhodian platinum, platinum-iron alloy, platinum, and palladian gold; b) the tellurides — moncheite ($PtTe_2$), kotulskite (PdTe), merenskyite ($PdTe_2$) and some new, as yet undefined species; c) the sulphides —cooperite (PtS), braggite [(Pt,Pd)S] and vysotskite (PdS); and, d) the arsenides — sperrylite ($PtAs_2$), and several comlex, as yet undefined arsenides. Other associated opaque minerals include pyrite, chalcopyrite, pentlandite, pyrrhotite, chromite, magnetite, marcasite, violarite, graphite and gold.

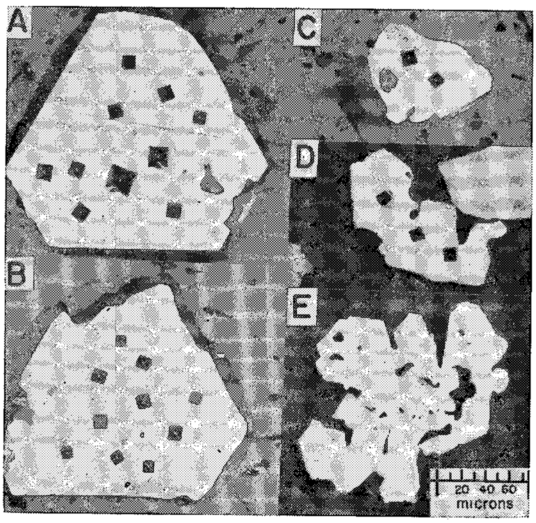

FIG. 1. Composite photomicrograph: A. platinian rhodium, gr. 1; B. rhodian platinum, gr. 2; C. rhodian platinum, gr. X; D. rhodian platinum, gr. 8; E. rhodian platinum, gr. 7.

Moncheite, braggite, and vysotskite have not been reported previously from the Stillwater Complex. This is only the second recognized occurrence of vysotskite, the first being described by Genkin & Zvyagintsev (1962) from the chalcopyrite-millerite ores of Noril'sk. The native alloys only will be described in this paper.

Rhodium

A single grain of rhodium was found and is characterized as a new mineral. The mineral is actually the variety platinian rhodium and the name rhodium and the mineral data were approved by the Commission on New Minerals and Mineral Names, IMA. The type material is attached to the end of a glass fibre with glyptal cement and preserved in the Royal Ontario Museum (M 33257).

Under reflected light, in air, the mineral is bright white and isotropic. In cross-section, platinian rhodium occurred as a 175 × 195 micron subhedral grain (Fig. 1A). Reflectance measurements (done in triplicate) are tabulated in Table 1. Micro-indentation hardness measurements gave $VHN_{30} = 165$ (136-194) for eight indentations.

Quantitative electron probe analysis showed the grain to be homogeneous and corresponding to the formula $Rh_{0.57}Pt_{0.43}$ (Table 2). The mineral is thus platinian rhodium and is named for the end member, rhodium. The probe data were first processed using the EMPADR VII program but were later reprocessed with the MAGIC program. The atomic proportions were the same in each case but the weight per cent total came to 102.2% with EMPADR and 101.3% with MAGIC. The latter total is reported in Table 2. All other analyses reported in Table 2 were

TABLE 1. REFLECTANCE MEASUREMENTS ON PLATINIAN RHODIUM AND RHODIAN PLATINUM (IN AIR)

Anal. No.	Composition	Area meas. (µm)	wavelength 470 nm	546 nm	589 nm	650 nm
1	$Rh_{.57}Pt_{.43}$	22 x 22*	75.2 (72.9-77.0)	72.6 (72.1-73.5)	73.3 (72.2-75.2)	75.7 (74.1-77.0)
2	$Pt_{.68}Rh_{.32}$	15 x 15*	70.7 (69.3-72.9)	70.1 (69.3-71.4)	70.7 (70.6-70.9)	73.8 (73.0-75.0)
4	$Pt_{.69}Rh_{.31}$	15 x 15**	69.0 (66.8-70.6)	69.1 (67.6-70.1)	70.5 (69.7-71.2)	72.8 (72.7-73.0)
5	$Pt_{.68}Rh_{.32}$	22 x 22*	71.1 (69.4-72.5)	71.7 (70.7-72.8)	72.4 (71.3-74.3)	75.2 (73.7-77.0)

* measured three times ** measured four times

TABLE 2. ELECTRON MICROPROBE ANALYSES OF PLATINIAN RHODIUM, RHODIAN PLATINUM, PLATINUM-IRON ALLOY, PLATINUM, AND PALLADIAN GOLD

	Elements Weight Per Cent										Atomic Proportions									
Mineral	Pt	Pd	Rh	Ir	Fe	Cu	Ni	Au	Ag	Total	Pt	Pd	Rh	Ir	Fe	Cu	Ni	Au	Ag	Σ
1. Platinian Rh,* gr. 1	59.6	--	41.7	--	--	--	--	--	--	101.3	0.43	--	0.57	--	--	--	--	--	--	*1.00*
2. Rhodian Pt,* gr. X	80.9	--	20.1	--	--	--	--	--	--	101.0	0.68	--	0.32	--	--	--	--	--	--	*1.00*
3. Rhodian Pt, gr. 7	81.8	--	19.2	--	--	--	--	--	--	101.0	0.69	--	0.31	--	---	--	--	--	--	*1.00*
4. Rhodian Pt, gr. 8	81.8	--	19.7	--	--	--	--	--	--	101.5	0.69	--	0.31	--	--	--	--	--	--	*1.00*
5. Rhodian Pt, gr. 2	80.5	--	20.1	--	--	--	--	--	--	100.6	0.68	--	0.32	--	--	--	--	--	--	*1.00*
6. Pt-Fe alloy** gr. 4	88.4	--	--	n.d.	9.6	0.2	0.1	--	--	98.3	2.87	--	--	--	1.10	0.02	0.01	--	--	*4.00*
7. Pt-Fe alloy** gr. 5	89.4	--	--	n.d.	9.6	0.3	0.08	--	--	99.38	2.87	--	--	--	1.09	0.03	0.01	--	--	*4.00*
8. Pt-Fe alloy** gr. 6	90.9	--	--	n.d.	9.3	0.2	0.04	--	--	100.44	2.92	--	--	--	1.05	0.02	0.01	--	--	*4.00*
9. Platinum***, gr. 4	86.4	5.6	n.d.	9.3	n.d.	--	--	--	--	101.3	3.26	0.39	--	0.35	--	--	--	--	--	*4.00*
10. Palladian Au,* gr. 5	--	6.6	--	--	--	--	--	91.3	1.1	99.0	--	0.46	--	--	--	--	--	3.46	0.08	*4.00*
11. Palladian Au, gr. 9	--	7.3	--	--	--	--	--	90.3	4.8	102.4	--	0.48	--	--	--	--	--	3.21	0.31	*4.00*
12. Palladian Au, gr. 8	--	7.3	--	--	--	--	--	88.5	2.4	98.2	--	0.51	--	--	--	--	--	3.33	0.16	*4.00*

*grain *x*-rayed **Sb also not detected (n.d.) ***Ru, Os also not detected.

TABLE 3. *X*-RAY DIFFRACTION DATA FOR PLATINIAN RHODIUM, RHODIAN PLATINUM, AND PALLADIAN GOLD

	Platinian Rhodium[1] a = 3.856(1)			Rhodian Platinum[1,2] a = 3.886(1)			Palladian Gold[3] a = 4.047(1)Å		
hkl	*I*	d_{meas}	d_{calc}	*I*	d_{meas}	d_{calc}	*I*	d_{meas}	d_{calc}
111	6	2.227	2.226	9	2.242	2.243	10	2.328	2.336
002	3	1.927	1.928	4	1.942	1.943	7	2.021	2.023
022	5	1.362	1.363	5	1.373	1.373	6	1.431	1.431
113	5	1.162	1.162	7	1.172	1.172	8	1.219	1.220
222	1	1.112	1.113	2	1.122	1.122	3	1.166	1.168
004	2	0.9639	0.9640	2	0.9715	0.9715	1	1.010	1.011
133	7	0.8847	0.8846	8	0.8916	0.8915	6	0.9284	0.9284
024	8	0.8623	0.8622	9	0.8690	0.8689	6	0.9046	0.9049
224	10	0.7874	0.7871	10	0.7933	0.7932	8b	0.8259	0.8261

Intensities estimated, b = broad

1. Ni-filtered Cu radiation, 114.6 mm Gandolfi camera.
2. Gr. X, Table 1.
3. Ni-filtered Cu radiation, Gr. 5, Table 1, 57.3 mm Gandolfi

done with EMPADR since some checks with MAGIC differed insignificantly.

The *x*-ray powder pattern for platinian rhodium is given in Table 3 and the cell edge $a = 3.856(1)$Å is in good agreement with the expected linear relationship for Rh-Pt alloys (Fig. 2).

Rhodian platinum

Four grains of rhodian platinum were studied (Fig. 1-B, C, D, E). These are bright white under reflected light but have a pinkish tinge and are isotropic; they appear slightly less bright than the platinian rhodium. Reflectance measurements were made on three of the grains (Table 1) and the analyses for all four are given in Table 2. The relatively constant Pt:Rh ratio for all four grains is remarkable.

Micro-indentation hardness measurements with a 30 g weight were made on the largest grain to compare with platinian rhodium, and with a 20 g weight to compare with the smaller rhodian platinum grains. Grain No. 2, (anal. No. 5 in Table 2) gave $VHN_{30} = 181$ (167-203) for five indentations; hence it is slightly harder than the platinian rhodium. $VHN_{20} = 152$ (146-161) was obtained for five indentations of the same grain, while grain 8 (anal. No. 4 in Table 2) gave $VHN_{20} = 147$ (128-167) for three indentations and grain X (anal. No. 2 in Table 2) gave $VHN_{20} = 94$ and 135. The latter results are considered unreliable, probably because the grain was too small or too thin.

The *x*-ray powder pattern for rhodian platinum (grain X anal. No. 2 in Table 2) is compared with that of platinian rhodium in Table 3 and the mineral has the cell edge $a = 3.886(1)$Å. This cell edge value plots very well on the linear curve between Pt and Rh (Fig. 2).

To the authors' knowledge, this is the first report of an occurrence of rhodian platinum.

Platinum-iron alloy

Three grains of platinum-iron alloy were analysed and were also found to be remarkably consistent in their compositions, all being near

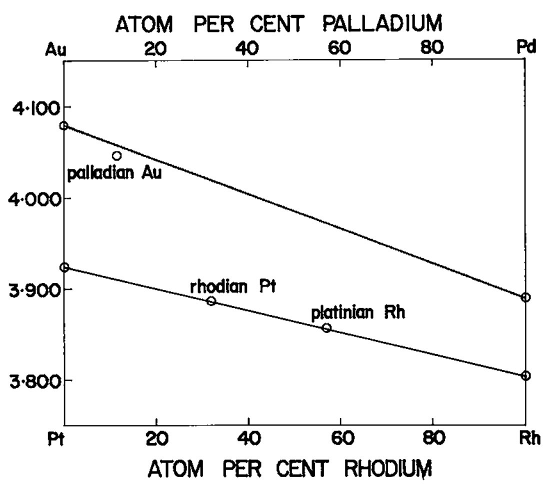

FIG. 2. Plot of composition vs. cell-edge for Pt-Rh and Au-Pd alloys. The values used for the pure end members are those in the PDF standards card file, Pt = 3.9231, Rh = 3.8031, Au = 4.0786, and Pd = 3.8898Å.

Pt_3Fe (Table 2). One of these grains (~30 × 80 microns) was removed from the section for *x*-ray diffraction and the pattern could be indexed on a cubic cell with $a = 3.863(2)$Å. The *x*-ray pattern, however, contains a few reflections which may only be indexed on a primitive cubic cell, in contrast to the face-centered cubic cell found for a Pt_3Fe grain from the Similkameen River (Cabri *et al.* 1973). This problem is still being studied.

Platinum

One 27 × 33 micron grain of platinum, containing a minor quantity of palladium and iridium, was analysed (Table 2). This composition, if plotted on a Pt-Pd-Ir triangular diagram, would lie in the Pt corner. Because the Pt content is more than 80 at.%, the mineral may be called native platinum by using the same criteria for nomenclature as proposed by Harris & Cabri (1973) and Cabri & Hey (1974).

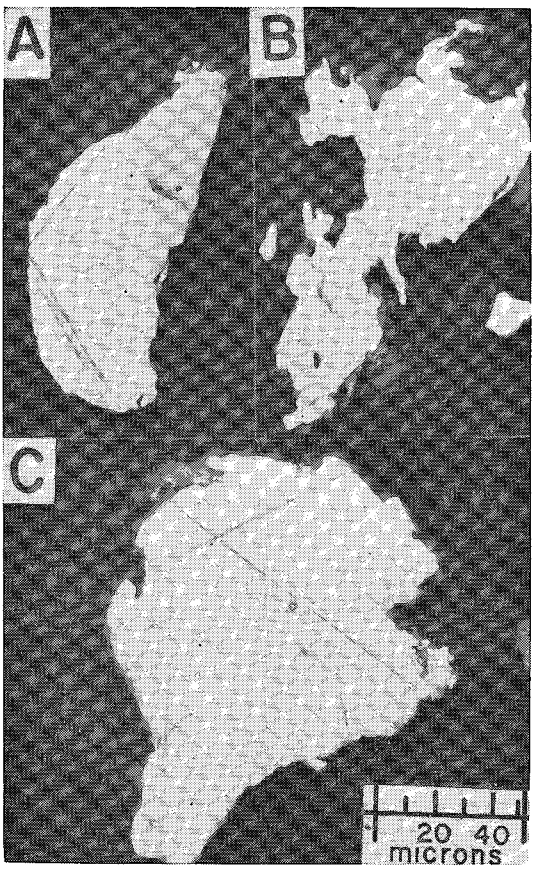

FIG. 3. Composite photomicrograph: A. palladian gold with vysotskite/braggite (grey), gr. 8; B. palladian gold, gr. 9; C. palladian gold, gr. 5.

Palladian gold

Three irregularly shaped grains of palladian gold were found and examined (Fig. 3). The grains are obviously soft and were difficult to polish. They are cream-coloured with a metallic pinkish cast under reflected light in air. They do not have the colour of gold and appear anisotropic under oil immersion. The reflectance at 589 nm is about 55% but this was not determined more accurately because of the poor polish. One grain was attached to a braggite or vysotskite grain (Fig. 3A), whereas the other two were free. The *x*-ray powder data for grain 5 (anal. No. 10 in Table 2) are given in Table 3 and the cell edge is plotted in Figure 2. To the authors' knowledge, no other face-centered cubic palladian gold native alloy has been reported in the modern literature. Dana (1892) reports on "*Palladium - Gold. Porpezite* Frobel. A variety from Porpez, Brazil, containing 10 p.c. of palladium, besides some silver, colour pale; also from Jacutinga and Condonga with 5 to 6 p.c. Pd." He further stated that a specimen from Taguaril, Minas Gerais gave Au 91.06, Pd 8.21. These reports, though on material determined as a bulk assay, appear to describe minerals very similar to the Stillwater palladian gold but are quite different from the orthorhombic $(Cu,Pd)_3Au_2$ mineral reported by Razin *et al.* (1971).

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