Canadian Mineralogist
Vol. 15, pp. 389-392 (1977)

PLATINUM-GROUP MINERALS FROM ONVERWACHT. III. GENKINITE, $(Pt, Pd)_4Sb_3$, A NEW MINERAL*

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Abstract

Genkinite, $(Pt,Pd)_4Sb_3$, is a new mineral found in a sample from the former Onverwacht mine, Transvaal. Under reflected light the mineral is pale brown or tan, with a yellowish tinge which is not apparent in oil. Bireflectance is not detectable in air with white light but the mineral is weakly bireflectant in oil. Genkinite is moderately to strongly anisotropic in both air and oil. Reflectance ranges from about 52% at 470nm to about 56% at 650nm. Micro-indentation hardness varies with composition: VHN_{25} =603 (578-612) for grains with 1.5 wt. % Rh. Genkinite is tetragonal, *a* 7.736(1), *c* 24.161(2)Å, with strongest diffraction lines 3.020(9) (025,008), 2.265(10) (134), 1.934(6) (040), 1.910(5) (0.2.11), 0.9043(5B) (2.6.18) and 0.9025(5B) (382). The calculated density is 9.256 g/cm³ for a crystal of composition $Pt_{2.45}Pd_{1.34}Rh_{0.15}Ni_{0.01}Sb_{2.99}As_{0.04}Bi_{0.02}$ with Z=8. The mineral has been synthesized and the experiments indicate that, though Pt>Pd, Pd is essential for structure.

Sommaire

La genkinite, $(Pt,Pd)_4Sb_3$, est un nouveau minéral trouvé dans un échantillon provenant de l'ancienne mine d'Onverwacht, au Transvaal. En lumière réfléchie, le minéral est brun pâle avec une pointe de jaune invisible dans l'huile. Biréflectance en lumière blanche non observable dans l'air, faible dans l'huile. Anisotropie, modérée à forte, soit dans l'huile ou dans l'air. Pouvoir réflecteur variant de 52% (470nm) à 56% (650nm). Microdureté variant avec la composition, VHN_{25}=603 (578-612) pour les grains les moins riches en Rh (1.5% en poids). La genkinite est tétragonale, *a* 7.736(1), *c* 24.161(2)Å. Raies de diffraction X les plus intenses: 3.020(9) (025,008), 2.265(10) (134), 1.934(6) (040), 1.910(5) (0.2.11), 0.9043(5B) (2.6.18) et 0.9025(5B) (382). Pour Z=8, on trouve D(calc) 9.256 pour un cristal de composition $Pt_{2.45}Pd_{1.34}Rh_{0.15}Ni_{0.01}Sb_{2.99}As_{0.04}$-$Bi_{0.02}$. La synthèse du nouveau minéral a été effectuée, et les expériences démontrent que le Pd est essentiel, bien qu'on ait Pt>Pd.

*Minerals Research Program, Processing Contribution No. 36

Introduction

During an investigation of a sample (~15× 20×35 mm) from the former Onverwacht platinum mine, Transvaal, the new mineral genkinite was found and characterized. Further details on the sample origin and the Onverwacht deposit are given by Cabri *et al.* (1977a).

Procedures

Sample preparation, reflectivity measurements, micro-indentation hardness measurements, X-ray diffraction procedures and electron probe analyses were as described previously (Cabri *et al.* 1977b) except for the use of the following X-ray lines and (standards): Pt$L\alpha$, Sb$L\alpha$ (synthetic Pt_3Sb_2); Rh$L\alpha$ (synthetic $Pt_{0.68}Rh_{0.32}$); Pd$L\alpha$ (metal); Cu$K\alpha$ (synthetic $Pd_{4.85}Cu_{0.15}Sb_2$); Bi$M\alpha$ (synthetic PdBiTe and Bi metal); As$K\alpha$ (synthetic InAs); and Ni$K\alpha$ (metal). Corrections were applied by using a slightly modified version of the EMPADR VII computer program of Rucklidge & Gasparrini (1969). Corrections were also applied for enhancement of Pd$L\alpha_1$ by Rh$L\beta_1$. Semi-quantitative analyses were made with an energy dispersive X-ray analyzer (EDX). Reflectance measurements were made on 10×10 micron areas.

Syntheses were made by reacting high-purity elements in evacuated silica-glass tubes. The charges were examined periodically and the contents were subjected to various grinding, pelletizing, and annealing operations. Pt_3Sb_2 and bulk compositions of $(Pt,Pd)_4Sb_3$ and $(Pt,Pd)_3Sb_2$ were synthesized at ~675°C. Synthesis of a bulk composition Pt_4Sb_3 was attempted at ~700°C.

Optical, Physical and Chemical Properties of Genkinite

Genkinite occurs as irregular grains ranging in size from less than 5 microns to about 165× 165 microns. It is associated with sperrylite, Pt-

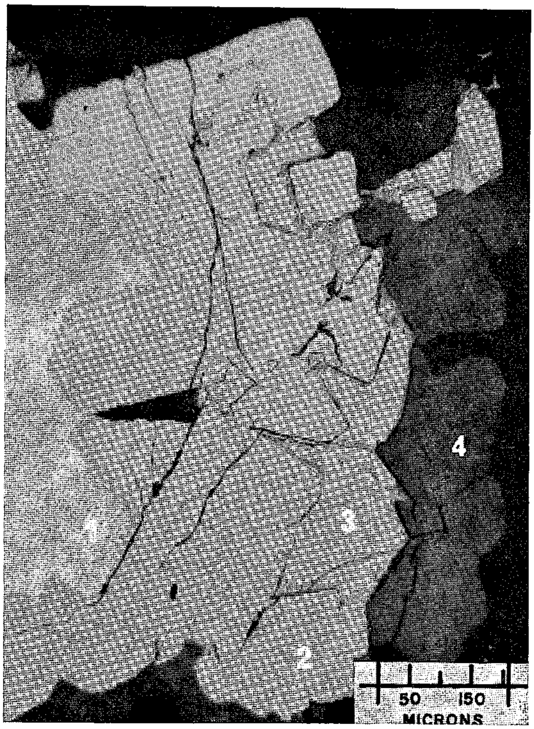

FIG. 1. Genkinite (3), with a typical rim of an undetermined oxidation product (darker grey), closely associated with platarsite (2) and Pt-Fe alloy (1). Chromite crystals (4) enclose the platinum-group minerals.

Fe-Cu-Ni alloys (Cabri *et al.* 1977a), platarsite (Fig. 1 and Cabri *et al.* 1977b), ruthenarsenite, stibiopalladinite, mertieite II, and an unidentified Pt-Pd-Rh oxide in a sample containing silicates and chromite. In polished section with white light genkinite is pale brown or tan with a yellowish tinge, moderately to strongly anisotropic from grey to brown, but bireflectance in air is not detectable to the human eye. In oil the yellowish tinge is not apparent, some grains are weakly bireflectant, and the anisotropism varies from moderate to strong, going from grey to extinction. With the analyzer at 2° off extinction position, the mineral goes from near extinction to brown, or from grey to brown. Reflectances in air in % (av. of 2 meas. of Rg' and Rp' on grain No. 5) are: 470nm 52.55, 51.7; 546nm 54.05, 53.5; 589nm 55.25, 54.6; 650nm 56.5, 56.2. The averages of 2 measurements on grain No. 2 are: 470nm 52.9, 51.9; 546nm 53.05, 52.4; 589nm 54.0, 53.5; 650nm 54.85, 54.5. Micro-indentation hardness gives VHN_{25}=603 (578-612) for grain No. 5, and VHN_{25}=677 (627-697) for grain No. 2 (five indentations on each grain).

Electron probe analyses of eight grains are given in Table 1. The ideal formula seems to be $(Pt,Pd)_4Sb_3$ with Pt>Pd. All analyses (calculated on the basis of seven atoms) are slightly metal-poor and antimony-rich within the range 0.02 to 0.05. Since the mineral contains seven or eight elements, such variations may be due to analytical error rather than to non-stoichiometry.

An X-ray powder pattern of crystal No. 4 was obtained with a 114.6 mm Gandolfi camera and Fe-filtered Co-radiation (Table 2). Crystals No. 2 and 4 were determined to be tetragonal by precession photography, and the indexed Gandolfi pattern gave a 7.736(1), c 24.161(2)Å. The space group could not be unequivocally assigned; it may be $P4_12_12$, $P4_122$, $P4_322$, $P4_32_12$, $P4_22_12$, or $P4_222$. The correct space group will have to be determined by a complete X-ray crystal-structure study. The calculated density for grain 4 is 9.256 g/cm³, assuming Z=8.

SYNTHESIS EXPERIMENTS

In the most recent study of the Pt-Sb system, Bahn *et al.* (1969) report five binary phases: $PtSb_2$, PtSb, Pt_3Sb_2, Pt_3Sb and Pt_4Sb. The need

TABLE 1. ELECTRON MICROPROBE ANALYSES OF GENKINITE

Anal. no.	Weight percent									Atomic proportions									
	Pt	Pd	Rh	Ni	Cu	Sb	Bi	As	Total	Pt	Pd	Rh	Ni	Cu	Σ	Sb	Bi	As	Σ
1	44.4	9.0	6.6	2.0	0.25	35.8	1.7	0.89	100.64	2.19	0.81	0.61	0.33	0.04	3.98	2.83	0.08	0.11	3.02
2	42.1	11.8	7.4	0.54	0.38	36.8	0.64	0.85	100.51	2.07	1.06	0.69	0.09	0.05	3.96	2.90	0.03	0.11	3.04
3	41.9	12.2	7.3	0.51	0.39	36.7	0.57	0.94	100.51	2.05	1.10	0.68	0.08	0.06	3.97	2.88	0.03	0.12	3.03
4	47.3	14.1	1.5	0.06	n.d.*	36.1	0.49	0.27	99.82	2.45	1.34	0.15	0.01	0.00	3.95	2.99	0.02	0.04	3.05
5	47.1	14.2	1.5	0.05	n.d.	35.7	0.65	0.21	99.41	2.45	1.35	0.15	0.01	0.00	3.96	2.98	0.03	0.03	3.04
6	45.6	14.6	1.9	0.16	n.d.	35.8	0.75	0.24	99.05	2.36	1.39	0.19	0.03	0.00	3.97	2.97	0.03	0.03	3.03
7	46.2	14.2	1.9	0.18	n.d.	35.9	0.81	0.32	99.51	2.39	1.34	0.19	0.03	0.00	3.95	2.97	0.04	0.04	3.05
8	47.7	13.7	1.5	0.05	n.d.	35.2	0.58	0.20	98.93	2.50	1.32	0.15	0.01	0.00	3.98	2.96	0.03	0.03	3.02

* n.d. = not detected

for probe standards close in composition to the unknown mineral, and the determination of whether or not Pd was essential, required some experimental work.

Pt_3Sb_2 was synthesized and the indexed X-ray powder-diffraction pattern was refined to give *a* 6.445(4), *b* 10.947(4), *c* 5.320(3)Å, in agreement with the data of Bahn *et al.* (1969). Impurities of less than 0.5 vol. % were present in the synthetic Pt_3Sb_2 and could not be identified, even with EDX. Attempts to synthesize Pt_4Sb_3 were unsuccessful; charges with this bulk composition gave a two-phase product consisting of Pt_3Sb_2 and PtSb, in agreement with the phase diagram of Bahn *et al.* It was thus confirmed that Pt_4Sb_3 did not occur as a binary phase in the Pt-Sb system, but that genkinite may be considered to be a *ternary* phase in the Pt-Pd-Sb system. Therefore, two charges were prepared with bulk compositions of $(Pt,Pd)_3Sb_2$ (19.3 wt. % Pd) and $(Pt,Pd)_4Sb_3$ (17.7 wt. % Pd;) these charges are referred to as A and B, respectively. The products of both charges consisted of a major phase with the general formula $(Pt,Pd)_4Sb_3$, and a minor phase. The major phase produced from A had the composition $Pt_{2.67}Pd_{1.26}Sb_{3.07}$, and the minor phase was $Pd_{4.70}Pt_{2.28}Sb_{3.02}$, or approximately $(Pd,Pt)_7Sb_3$. The resultant major phase from B had the composition $Pt_{2.38}Pd_{1.58}Sb_{3.04}$, and the minor phase was $Pt_{0.76}Pd_{0.23}Sb_{1.01}$, or (Pt,Pd)Sb. The $(Pt,Pd)_4Sb_3$ phases from both experiments had the same powder patterns as that of genkinite. Indexing of one pattern gave *a* 7.736(2), *c* 24.152(9)Å, in good agreement with the cell dimensions of genkinite.

These experiments indicate that genkinite is $(Pt,Pd)_4Sb_3$ with Pt>Pd, and that Pd may be essential. The amount of Pd required for the genkinite structure has not been determined, but natural material ranges between 0.81 to 1.39 Pd, based on seven atoms per formula unit.

Discussion

Tarkian & Stumpfl (1975) described an unnamed mineral $(Pt,Pd)_3Sb_2$ from the Driekop deposit. The qualitative optical properties of their mineral are similar to those of genkinite, and their reported microprobe analyses can be recalculated to give $(Pt_{2.38}Pd_{1.66})_{\Sigma=4.04}(Sb_{2.77}Sn_{0.13}Bi_{0.06})_{\Sigma=2.96}$, $(Pt_{2.38}Pd_{1.66})_{\Sigma=4.04}(Sb_{2.75}Sn_{0.13}Bi_{0.08})_{\Sigma=2.96}$ and $(Pt_{2.37}Pd_{1.64})_{\Sigma=4.01}(Sb_{2.78}Sn_{0.13}Bi_{0.08})_{\Sigma=2.99}$ or $(Pt,Pd)_4(Sb,Sn,Bi,As)_3$. The reflectance values reported for their mineral are close to those of genkinite at 546 and 650nm, but the differences at 470 and 589nm are large enough to give different shapes to the reflectance curves of the two minerals. Moreover, the reported micro-indentation hardness of the unnamed $(Pt,Pd)_3Sb_2$ is about half that of genkinite. Speculation that the unnamed $(Pt,Pd)_3Sb_2$ [or $(Pt,Pd)_4(Sb,Sn,Bi,As)_3$?] is an Sn-bearing, Rh-free variety of genkinite is attractive, but proof of this requires confirmatory X-ray data.

TABLE 2. X-RAY POWDER DATA FOR GENKINITE

I	d_{obs}	d_{calc}	*hkl*	*I*	d_{obs}	d_{calc}	*hkl*
3	3.47	3.48	023	½	1.231	1.230	165
9	3.020	3.020	025,008	1	1.215	1.215	358
½	2.816	2.813	018,125	2	1.202	1.208	00.20
2	2.454	2.455	033	1	1.191	1.190	04.16
½	2.367	2.371	034	1	1.185	1.185	454
10	2.265	2.267	134	2	1.169	1.169	25.12
2	2.204	2.205	029	2	1.140	1.141	363
4	2.146	2.145	230	1	1.129	1.128	13.19
4	2.120	2.121	129	½	1.113	1.113	269
1	2.073	2.073	233	½	1.089	1.089	552
½	2.013	2.013	00.12	½	1.059	1.059	369
½	1.979	1.981	12.10	4B	1.012	1.013	02.23
6	1.934	1.934	040	1	1.002	1.002	278
5	1.910	1.910	02.11	½	0.9641	0.9639	082
½	1.854	1.854	142	3	0.9478	0.9477	184
1	1.812	1.811	22.10	1	0.9405	0.9403	086
½	1.726	1.725	241	½	0.9312	0.9313	44.19
2	1.630	1.629	245	3	0.9290	0.9292	46.13
½	1.467	1.468	23.12	3	0.9205	0.9206	45.17
1	1.389	1.389	157	½	0.9132	0.9137	286
1	1.366	1.367	440	4	0.9089	0.9091	662
2	1.357	1.356	158	2	0.9062	0.9060	663
½	1.294	1.295	446	5B	0.9043	0.9042	26.18
½	1.285	1.285	15.10	5B	0.9025	0.9029	382
4	1.265	1.265	34.11	4B	0.8969	0.8969	572
3	1.244	1.244	164				

Nomenclature and Preservation of Type Material

The name genkinite and the mineral, $(Pt,Pd)_4Sb_3$ with Pt>Pd, have been approved by the Commission on New Minerals and Mineral Names, I.M.A. The name is for Dr. A. D. Genkin, Soviet mineralogist, for his important contributions to the mineralogy and geochemistry of the platinum-group elements.

Polished sections containing type material are preserved in the Royal Ontario Museum (No. M34681), Toronto; U.S. National Museum, Smithsonian Institution (No. 136485), Washington, D.C.; and the Mineralogical Museum of the Academy of Sciences (No. N79000) Moscow. Two grains, mounted on glass fibres, are in the collection of the Crystal Structure Laboratory, CANMET. The remainder of the hand specimen (No. 1949) is in the Pinch Mineralogical Museum.

Acknowledgments

The authors are grateful to Mr. W. W. Pinch for the sample, to Dr. D. C. Harris for helpful discussions about the stoichiometry of genkinite, to Dr. T. T. Chen for assistance with the X-ray data, and to Mr. P. Carrière for the photomicrograph. The authors are also grateful to Mr. A. J. Criddle (British Museum), Dr. B. F. Leonard (U.S.G.S.), and Mr. P. Mihalik (Amax) for critical reviews of the manuscript, but absolve them for any errors remaining.

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Manuscript received February 1977, emended March 1977.