NEW PALLADIUM MINERALS FROM NORIL'SK, WESTERN SIBERIA

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ABSTRACT

Two new palladium minerals from Noril'sk, Pd_3Pb and Pd(Bi, Pb), are described. Pd_3Pb is cubic, with $a = 4.02_5$ Å, and with space group $Pm3m$. It is white in reflected light, and has a high reflectivity which varies from about 60 to 67% over the wavelength range of 4500 to 6560 Å. The mean Vickers Hardness Number for a 15 g load is 279. Pd(Bi, Pb) is anisotropic; colours are grey to pale brown in oil. An estimate of the Vickers Hardness Number, using the pseudo-Becke line, indicated a value somewhere between 201 and 276 for a 50 g load.

INTRODUCTION

Pd_3Pb and Pd(Bi, Pb) are new minerals discovered in a small specimen measuring about 4 cm to a side, from Noril'sk, Siberia, kindly sent to Cabri by the Leningrad Mining Institute Museum. A personal communication from A. D. Genkin, following the discovery, stated that he has independently described what is probably the Pd_3Pb mineral*. The Noril'sk group of deposits, consisting mostly of ores of the chalcopyrite-pentlandite-pyrrhotite type, occur on the western boundary of the Siberian plain. The ores are associated with intrusives of differentiated gabbro-diabases, cutting rocks of the Tungusk sandstone-schist strata

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*"Zvyagintsivite—a natural intermetallic compound of palladium, platinum, lead, and tin" by A. D. Genkin, I. V. Muravyeva, & N. V. Troneva, appeared in *Geology of Ore Deposits*, 1966, #3, p. 94–100 while our paper was in press. The differences in composition and description between zvyagintsivite and our mineral are greater than anticipated and worthy of further comment.

1. The zvyagintsivite electron-probe microanalysis adds up to 102½% and the atomic ratio of 2.7:1 is closer to 5:2 than 3:1.
2. The association of zvyagintsivite with ferro-platinum and pentlandite is in contrast to our mineral which is associated with copper-iron sulphides, silver-gold alloy, and Pd(Bi, Pb) alloy and was never found within pentlandite.
3. Pt and significant amounts of Sn are present in zvyagintsivite, whereas Pt and Sn were not detected in our mineral; however Au was.
4. The composition given by Genkin *et al.* (0.54 Pb vs. 0.46 Sn at.%) approaches the mid-point in a series Pd_3Pb–Pd_3Sn. They have suggested a similarity to the Pd_3Pb end member based on "composition" and *x*-ray data and described it as a natural inter-metallic compound of Pd, Pt, Pb, and Sn. However, they have not stated whether the name zvyagintsivite applies to their specific intermetallic compound or to an end member of the Pd_3Pb–Pd_3Sn series.

(Permian) which include some layers of coal. The three main types of ores are disseminated ores in picritic and taxitic gabbro-diabases, disseminated ores in the underlying rocks, and sulphide veins. The minerals of the platinum group are most common in the sulphide veins, and those richest in platinum group minerals are the chalcopyritic veins (Zontov, 1959).

The associated minerals in the sample consist principally of cubic chalcopyrite (Bud'ko & Kulagov, 1965; and Cabri, in preparation),

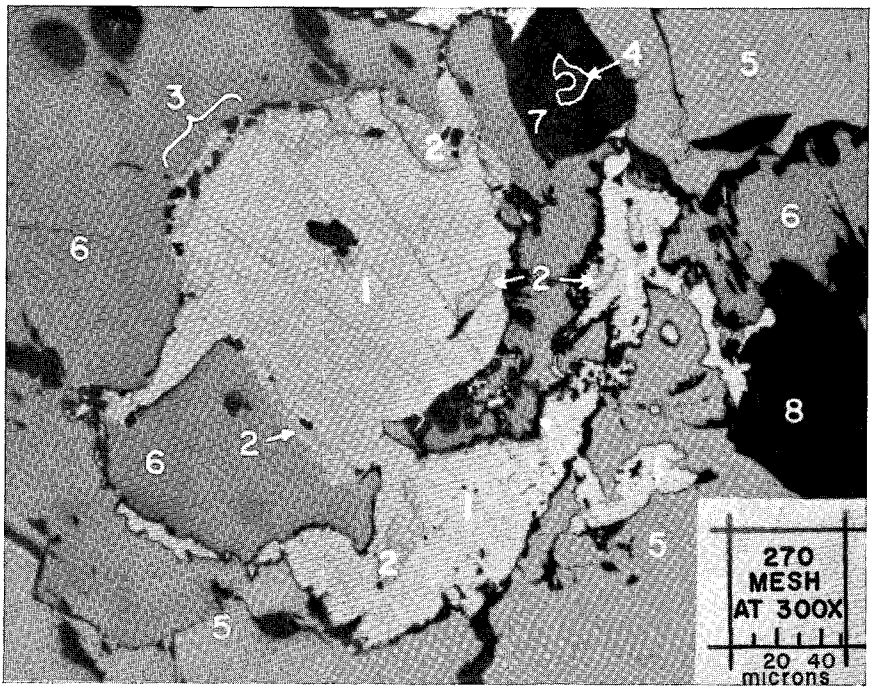

FIG. 1. Photomicrograph of grain #1. 1 = Pd_3Pb, 2 = Pd(Bi, Pb), 3 = etch pits of former (Ag, Au) alloy, 4 = magnetite, 5 = chalcopyrite (cubic), 6 = cubanite, 7 = gangue, 8 = valleriite.

cubanite, pentlandite, minor magnetite and valleriite, and a (Ag, Au) alloy. Pd_3Pb is the more common of the two palladium minerals, occurring as irregular grains, from about 250 to less than 4 microns, and veinlets as long as 120 microns. It usually occurs within the copper sulphides, and also within valleriite and magnetite, but was not found in the pentlandite (Figure 1). (Ag, Au) alloy grains were mostly found at the periphery of Pd_3Pb grains. The Pd(Bi, Pb) mineral was always found within the Pd_3Pb mineral (Figure 1).

A polished section containing both minerals has been deposited with the Systematic Reference Series, National Mineral Collection, Ottawa.

Procedures

Pd_3Pb was synthesized from the elements (J.M. 940 Pd sponge lot #10538 and J.M. 561 Pb rod lot #20807) by heating in an evacuated silica glass tube. The charge was heated at ~700 °C for one hour, then at ~1165 °C for 64 hours, and finally annealed at ~850 °C for 72 hours. A slight excess of Pb (0.04 wt %) was employed, since Ruer (1907) indicated that Pd_3Pb has a wide homogeneity range (39.36–35.3 wt % Pb; stoichiometric Pd_3Pb has 39.36 wt % Pb).

X-ray powder diffraction data were obtained by means of a 114.6 mm Debye-Scherrer camera, using nickel-filtered copper radiation. The *d*-values were obtained from the film measurements, corrected for shrinkage, and these values were used to calculate the cell parameters for which the average value is given.

The reflectivity measurements were made using a tungsten standard kindly provided by Dr. E. N. Cameron to Dr. E. H. Nickel of the Mines Branch, Mineral Sciences Division. The reflectivity values for the tungsten standard (Figure 2) are from Cameron & Carpenter (1964). The reflectivity apparatus consisted of a Leitz Ortholux-Pol research microscope, equipped for incident light, and a Leitz MPE microscope photometer. The microscope objectives employed had magnifications of 16× and 20×, and numerical apertures of 0.40 and 0.45, respectively. The stabilization of the light source was similar to that described by Bowie & Taylor (1958) and the light was monochromatized by a continuous monochromatic interference filter of the type Veril B200 manufactured by Jena^{er} Glaswerk Schott and Gen. and supplied by Bellingham and Stanley Ltd., London, England. This device has been described by Harrison & Day (1963).

The microhardness measurements were made with a Leitz Durimet microhardness tester, following the general procedure described by Young & Millman (1964). Microhardness indentations were made in a circular pattern wherever possible, and the mean of the two diagonals was the value taken for each indentation.

The samples, mounted in cold-setting plastic, were polished on lead laps, using various diamond abrasives down to $\frac{1}{4}$ micron, and finally polished on a slow-turning cloth lap, using a dilute chromic acid solution. It was later discovered that this chromic acid solution reacted rapidly with the silver-gold alloy, leaving small black pits in its place.

An Elion electron-probe microanalyzer was used for the investigation.

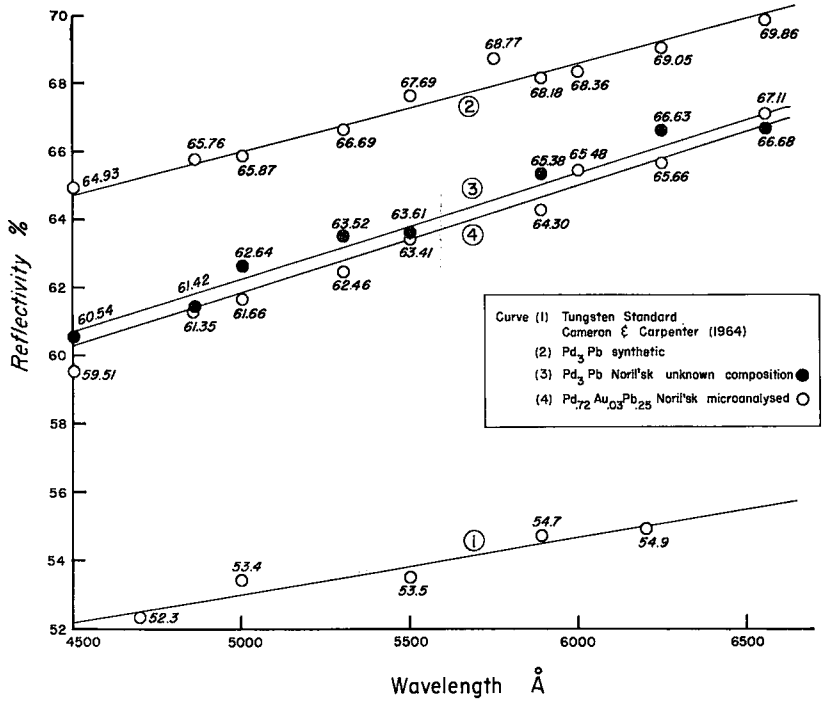

FIG. 2. Reflectivity curves for tungsten standard and for synthetic and natural Pd_3Pb.

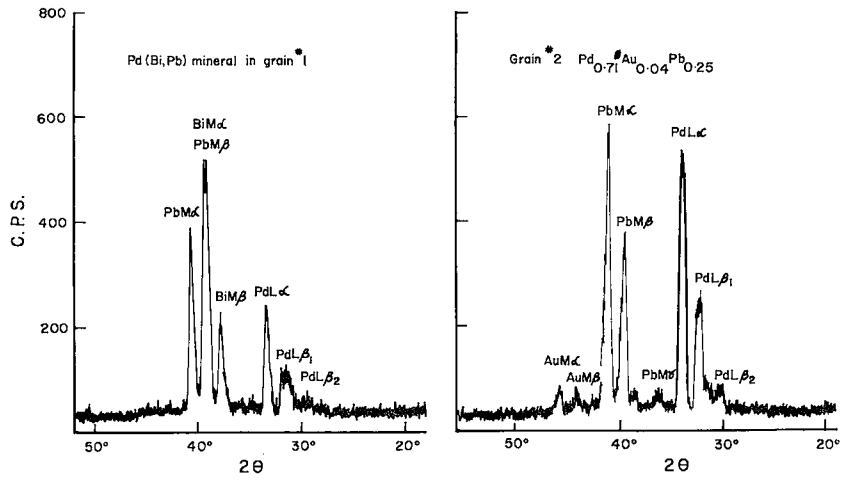

FIG. 3. Qualitative spectrometer scans for the Pd_3Pb and Pd(Bi, Pb) minerals.

Qualitative spectrometer scans (Figure 3) served to identify the elements present in the minerals. Intensities of characteristic x-ray lines of the elements were then measured relative to the intensities emitted by pure metals. The x-ray lines used were Pd $L\alpha$, Pb $M\alpha$, Bi $M\beta$, and Au $M\alpha$. Corrections for matrix effects were applied following the method suggested by Birks (1963), using mass absorption coefficients based on values given by Smith (1965, p. 840). All work was performed at an excitation voltage of 30 kv.

The responsibility for the work reported in this paper is divided between the authors as follows: R. J. Traill is responsible for the electron-probe microanalysis, and L. J. Cabri is responsible for the remainder of the investigation and for the preparation of this paper.

The Pd_3Pb Mineral

Chemical composition

The chemical composition of the Pd_3Pb mineral was established by means of the electron-probe microanalysis of two individual mineral grains, both of which were shown to be homogeneous. The results, shown in Table 1, indicate rather similar compositions, although there is an appreciable difference in the gold content. X-ray scanning pictures for the Cu-, Pd-, Pb- and Bi-radiations are shown in Figure 4.

Table 1. Electron-probe Analyses of Pd_3Pb

	Pd%	Pb%	Au%	Total %	Formula
Grain #1	57.3	38.7	3.6	99.6	$Pd_{0.72}Au_{0.03}Pb_{0.25}$ or $(Pd,Au)_3Pb$
Grain #2	55.6	38.0	6.0	99.6	$Pd_{0.71}Au_{0.04}Pb_{0.25}$ or $(Pd,Au)_3Pb$

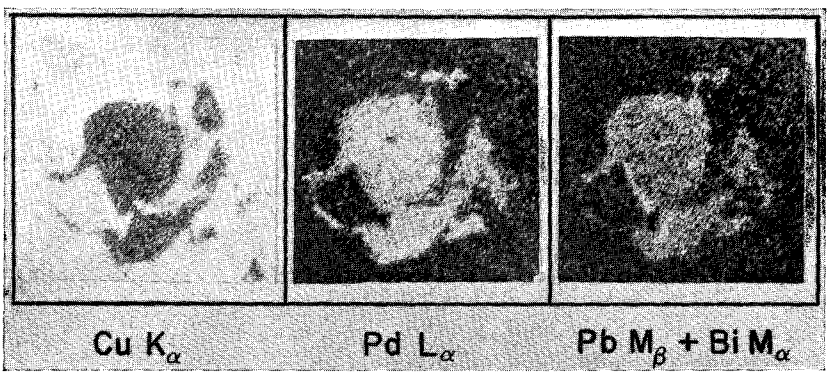

Fig. 4. X-ray scanning pictures of grain #1 for Cu-, Pd-, Pb- and Bi-radiation.

Both grains of Pd_3Pb were closely associated with the silver-gold alloy (Figure 1). That associated with grain #2 was found to have a Ag:Au ratio of 65:35 by comparison with 70:30 and 60:40 synthetic silver-gold alloys. Grain #1 was also host to the Pd(Bi,Pb) mineral.

X-ray diffraction analysis

X-ray powder patterns of the natural Pd_3Pb and the synthetic Pd_3Pb correspond closely to each other (Table 2), and the unit cells calculated

TABLE 2. *X*-RAY POWDER DIFFRACTION DATA FOR Pd_3Pb

	Natural Pd_3Pb Noril'sk			Synthetic Pd_3Pb	
hkl	*I**	*d*(meas.)	Extra phases	*I**	*d*(meas.)
100	1	4.01_8		1	4.00
	1	3.23	cubanite		
	3	3.04	chalcopyrite		
110	1	2.84		2	2.84
111	10	2.32		10	2.32
200	8	2.01		8	2.01
	2	1.86	cubanite		
	1	1.78	cubanite		
210				2	1.80
211				2	1.644
220	7	1.424		7	1.423
221, 300				w	1.342
310				w	1.272
311	6	1.214		9	1.215
222	3	1.163		4	1.163
320				w	1.117
321				w	1.077
400				3	1.007
410				w	0.973
330, 411				w	0.951
331	d	0.923		b, d 6	0.923
420	d	0.901		b, d 5	0.900
421				w	0.878
422	d	0.822		b, d 4	0.823
	av.a = 4.02_5Å			av.a = 4.02_4Å	

*Relative intensities estimated on a scale of 10. The intensities marked w, b, and d are for weak, broad, and diffuse reflections respectively.

from the *x*-ray data are in good agreement with that reported by Nowotny, Schubert & Dettinger (1946). They reported that synthetic Pd_3Pb has the cubic Cu_3Au structure with a = 4.021 Å, and this structure belongs to the $Pm3m$ space group. (They actually reported $a = 4.013_5$ Å but we have assumed that this is in kX units).

Specific gravity measurements on six grains of synthetic Pd_3Pb gave

an average value of 13.32. This indicates one formula weight per cell since it is close to the theoretical specific gravity of 13.41 for $Z = 1$.

Optical properties

In polished section, Pd_3Pb appeared bright white when compared with the surrounding sulphides, but the silver-gold alloy is whiter, giving a very faint grey or brownish cast to the palladium mineral. Anisotropism could not be detected in oil under crossed nicols.

Reflectivity measurements were made in air on synthetic Pd_3Pb and on two grains of natural Pd_3Pb. One of the latter was grain #1 (Table 1) and the other was from a different polished section which had not been microanalyzed. The reflectivity values are shown in Figure 2, and straight lines were drawn through the points by eye. A scratch-free polish was unobtainable on the natural grains, but this was very closely approached in the case of the synthetic phase. This probably accounts for the lower reflectivity of the natural grains, though the effect of the varying, and in one case unknown, amounts of gold on the reflectivity cannot be assessed. All but one point plotted for the synthetic phase represent the average values obtained for at least two separate determinations, and in some cases as much as five. Each determination was arrived at by alternately measuring the reflectivity of the sample and standard three times in quick succession. Curve 3 is the result of two determinations per point, while curve 4 represents only one set of determinations. The scatter of individual points about the curves in all cases compares favorably with the standard curve for tungsten, provided by Cameron & Carpenter (1964).

Hardness

The Vickers microhardness data on natural Pd_3Pb, shown in Table 3, were obtained from two grains in a polished section which were not microanalysed. Grain #3 was the same one which gave the reflectivity curve #3.

TABLE 3. VICKERS MICROHARDNESS DATA FOR Pd_3Pb

	Range of HV, in kg/mm²	Mean HV, in kg/mm²	Standard deviation	No. of indentations measured
Synthetic Pd_3Pb (50 g load)	241–276	256	11 (4%)	9
Synthetic Pd_3Pb (15 g load)	249–318	279	19 (7%)	10
Grain #3 (15 g load)	241–301	278		6
Grain #4 (15 g load)	252–318	280		3

The indentations were free of fracturing and were very nearly straight with a slight concave tendency. The effect of the gold content on the microhardness is not known.

Etch reactions

Reactions with standard etch reagents were made only on the synthetic phase. These are indicated in Table 4. In all cases the reagent was allowed one minute for the reaction, except for aqua regia which reacted too rapidly.

TABLE 4. REACTIONS WITH STANDARD ETCH REAGENTS FOR SYNTHETIC Pd_3Pb

HNO_3 1:1	+	Pale brown tarnish, iridescent at edges. Tarnish rubs off easily, leaving clean but etched surface.
HCl 1:1	+	Very pale brown stain.
KCN 20%	+	Extremely pale brown stain.
$FeCl_3$ 20%	+	Quick reaction, brown-black etch and stain.
$HgCl_2$ 5%	−	
KOH 40%	−	
Aq.Reg.	+	Rapid reaction with effervescence, etches and stains brown.

THE Pd(Bi, Pb) MINERAL

Chemical composition

Quantitative microanalysis of this mineral was performed on grains within the Pd_3Pb grain #1 (Figure 1). The complete analysis gave the following: Pd—33.1%, Bi—36.4%, and Pb—29.0%, total 98.5%. This corresponds to $Pd_{0.50}Bi_{0.28}Pb_{0.22}$ or Pd(Bi, Pb).

Optical properties

The Pd(Bi, Pb) mineral appears white in oil with a greyish tinge when compared with Pd_3Pb. Under crossed nicols it is moderately anisotropic, with colours from grey to a pale brown in oil, and no bireflectance could be ascertained. The narrow width of the grains, as shown in Figure 1, made reflectivity data difficult to obtain.

Hardness

No microhardness measurements were made, because the grains available were too few and too small. However, an estimate of the hardness was made by use of the pseudo-Becke line. This mineral proved to be harder than cubanite but softer than Pd_3Pb, thus probably indicating a Vickers microhardness between 201 and 276 kg/mm^2 at a 50 g load when using the minimum microhardness data for cubanite (Young & Millman, 1964) and the present highest value for synthetic Pd_3Pb.

Discussion

The only mineral with a composition near Pd_3Pb, reported in the literature at the time of writing, to the authors' knowledge, is Mineral #5 of Borovskii *et al.* (1959) and Genkin (1959). They gave the composition from microanalysis as Pd_4Pb with about 1% Ag. This was based on one determination and there was no mention of correction for selective absorption of excitation. Furthermore, there is no such compound reported in the synthetic Pd-Pb system; and, from our experience, it would be very difficult to detect the small amount of silver reported, because of interference from the major elements. Genkin (1959) reports this mineral to have a clearly expressed brownish tint, especially in contrast to sperrylite and galena. It was reported to have a reflecting power of about 65% and to be weakly anisotropic (bluish grey to brownish red). There are enough similarities to indicate that they may have been examining Pd_3Pb, but the data are not conclusive.

The only mineral reported in the literature approaching the Pd(Bi, Pd) mineral is the Mineral C described by Hawley (1962, p. 95–96). However, this mineral was reported to be harder than niccolite, and should therefore be much harder than the Pd(Bi, Pb) mineral.

It is interesting to note that both analysed Pd_3Pb grains had some gold, but no silver, substituting for palladium, even though they were in contact with the silver-gold alloys and in spite of the fact that there is complete solid solution in the synthetic Pd-Ag system (Rosenhall, 1935).

It is also interesting to note the results of numerous *x*-ray fluorescence and emission spectroscopic analyses on the bulk sulphide ore and sulphide mineral fractions. Emission spectroscopy revealed the presence of Ag, Pb and Cr besides the major elements, and Pd, Pt, Ga, Ge, Zn, Au, Sb, Bi, As and Hg were sought but not detected. *X*-ray fluorescence revealed Ag, Pd, Pb, and Zn, in addition to the major elements, but no Pt, Au, Rh, Ir, Os, Ge, Sn and Ga were detected. This confirms the difficulty of detecting trace amounts of some platinum group elements (and others) by routine trace element analyses, as was discussed by Edwards *et al.* (1942).

Acknowledgments

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