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CABRIITE Pd_2SnCu, A NEW SPECIES IN THE MINERAL GROUP OF PALLADIUM, TIN AND COPPER COMPOUNDS

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Abstract

Cabriite Pd_2SnCu is a new mineral species found in massive mooihoekite (putoranite) copper-nickel ore of the Oktyabr'sk deposit (Noril'sk district, USSR). It occurs as 200-μm grains, locally in association with sperrylite, paolovite, sobolevskite and polarite. Under reflected light, the mineral is bright pink with a lilac tinge, weakly bireflectant and strongly anisotropic. Reflectance in air at 580 nm: R_2 = 56.0%, R_1 = 47.4%. Micro-indentation hardness varies from 258 to 282 kg/mm^2. Cabriite is orthorhombic, $a \simeq b \simeq 7.88(5)$, $c \simeq 3.94(2)$ Å. The strongest diffraction lines [d in Å (I) (hkl)] are: 2.29(10) (221), 2.17 (9) (230,301), 1.840(3b) (330,112), 1.434(3b)(151), 1.230(8) (161,450,502,342,123), 1.217(4) (152), 1.182(3) (223,261). The calculated density is 10.7 g/cm^3 for the ideal composition with Z = 4. The analogue was synthesized in a study of the system Pd_3Sn - Cu_3Sn.

Keywords: cabriite, new mineral species, palladium, copper, tin, Oktyabr'sk, Noril'sk, USSR.

Sommaire

La cabriite Pd_2SnCu est une nouvelle espèce qui se trouve dans la mooihoekite (putoranite) massive du minerai de cuivre-nickel du gisement d'Oktyabr'sk (région de Noril'sk, URSS). Elle se présente en grains atteignant 200 μm, associés en certains endroits à la sperrylite, la sobolevskite et la polarite. En lumière réfléchie, elle est d'un rose vif à nuance lilas, de faible biréflectance, mais de forte anisotropie. Pouvoir réflecteur dans l'air: R_1 = 47.4% R_2 = 56.0% (580 nm). Microdureté 258 à 282 kg/mm^2. La cabriite est orthorhombique avec $a \simeq b \simeq$ 7.88(5), $c \simeq 3.94(2)$ Å. Raies de diffraction X les plus intenses [d en Å(I) (hkl)]: 2.29(10) (221), 2.17(9) (230,301), 1.840(3b) (330,112), 1.434(3b) (151), 1.230(8) (161,450,502,342,123), 1.217(4) (152), 1.182(3) (223,261); D(calc.) 10.7 pour formule idéale et Z = 4. Sa synthèse a été effectuée lors de l'étude du système Pd_3Sn - Cu_3Sn.

Mots-clés: cabriite, nouvelle espèce minérale, palladium, étain, cuivre, Oktyabr'sk, Noril'sk, URSS.

Introduction

A mineral of composition Pd_2SnCu has been found in the massive mooihoekite–putoranite ore of the Oktyabr'sk deposit in the Noril'sk area, USSR. In this ore, it is one of the most widespread of the palladium minerals. Palladium–platinum–tin minerals such as atokite Pd_3Sn, paolovite Pd_2Sn and rustenburgite Pt_3Sn are characteristic of the platinum-group-element (PGE) mineralization in the copper–nickel sulfide deposits of the Noril'sk area. In addition, stannopalladinite Pd_3Sn_2(?), found by Maslenitskii *et al.* (1947), taimyrite, described by Begizov *et al.* (1982) as $(Pd,Cu,Pt)_3Sn$ and a number of unnamed platinum-group minerals (PGM) were reported in numerous papers by A.D. Genkin and coauthors, by L.V. Razin and by O.E. Yushko-Zakharova (references listed in Cabri 1981). Most of these unnamed PGM contain platinum as well.

Though the Pd(Pt)–Sn–Cu minerals commonly occur as large grains (0.1–0.2 mm), they have not been sufficiently studied. At present there is no unanimous opinion concerning the number of Pd–Sn–Cu minerals and their composition. Resolution of the problems relating to the composition and properties of these minerals is not possible without using data on their synthetic analogues, such as was done in the Pd–Sn–Cu system, where study of the pseudobinary section Pd_3Sn–Cu_3Sn established the number of ternary phases that are analogues of minerals (Evstigneeva & Nekrasov 1980).

This paper, dedicated to the description of the new mineral *cabriite,* makes use of the results of an investigation of the synthetic analogue of cabriite, Pd_2SnCu, one of the low-temperature phases in the system Pd–Sn–Cu. More detailed data on this system

TABLE 1. REFLECTANCE DATA FOR CABRIITE

	nm	440	460	480	500	520	540	560	580	600	620	640	660	680	700	720	740
1	R_2	43.0	43.4	44.7	46.5	48.4	50.0	51.7	53.2	55.2	57.2	59.4	61.9	64.5	67.0	69.3	71.9
	R_1	42.4	43.0	44.0	45.5	46.8	48.2	50.0	51.4	53.2	55.0	57.2	59.6	62.0	64.8	67.3	70.0
2	R_2	39.8	40.5	41.6	43.0	44.7	46.1	47.9	49.8	51.7	53.7	56.1	58.4	61.0	63.6	64.2	69.0
	R_1	39.2	39.4	40.1	41.3	42.7	43.9	45.2	46.5	48.4	50.0	52.3	54.5	56.8	59.2	61.9	64.5
3	R_2	44.5	45.1	46.5	48.3	50.2	52.0	54.0	56.0	58.2	60.4	63.0	65.5	68.0	70.2	72.4	74.5
	R_1	42.5	42.4	42.5	43.2	44.0	45.0	46.0	47.4	49.0	51.0	53.3	56.0	58.3	61.1	63.5	66.4

Note: The sample numbers correspond to the numbers in Table 2.

and minerals are found in other papers, in particular that of Evstigneeva & Nekrasov (1980).

Optical, Physical and Chemical Properties

Individual cabriite grains, obtained from samples of mooihoekite and putoranite ores, are white with a slight greyish tinge. The brightness of the pink color changes depending on the host minerals. Bireflectance in air is detectable, and under crossed nicols, cabriite grains are strongly anisotropic. The anisotropism varies from greyish brown to golden colors. Cabriite characteristically exhibits a shreddy-aggregate texture, and individual grains are polysynthetically twinned.

Reflectance values over the range 440 to 740 nm, measured with respect to a WTiC standard, are presented in Table 1, and the reflectance spectra are shown in Figure 1. Optical properties of synthetic Pd_2SnCu are identical to those of cabriite (Fig. 1).

Micro-indentation hardness of cabriite was measured with a PMT-3 instrument calibrated with respect to NaCl(H_{NaCl} = 19 kg/mm^2 at P = 5 g). The range of values obtained was between 258 and 282 kg/mm^2 (P = 50 g), and the average of six measurements is 272 kg/mm^2. Synthetic Pd_2SnCu gave a somewhat higher range of values, 329–440 kg/mm^2, for the same conditions. The discrepancy must be due for a finer twin-intergrowth structure of the synthetic phase.

The composition of cabriite was determined with a Cameca MS-46 microprobe, operated with an accelerating voltage of 15–35 kV and probe current of 10–150 nA. The pure elements Pd, Sn, Cu, Pt, Ag and Sb were used as standards. The following X-ray lines were used: $K\alpha_1$ for Cu, $L\alpha_1$ for Ag, Pd, Pt, Sn and Sb. Corrections were made for the enhancement of Pd$L\beta$ by Ag$L\alpha$ and Sn$L\beta$ by Sb$L\alpha$. The chemical composition of several cabriite grains, as well as that of two grains of its synthetic analogue, is given in Table 2.

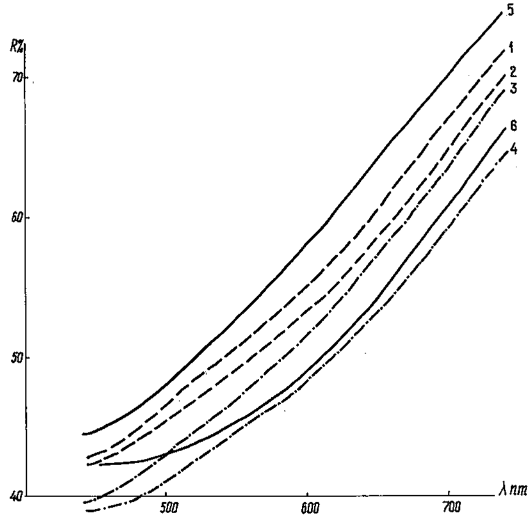


FIG. 1. Reflectance spectra of cabriite and Pd_2SnCu: 1 R_2, 2 R_1 (no. 1, Table 2), 3 R_2, 4 R_1 (no. 2, Table 2), 5 R_2, 6 R_1 (no. 3, Table 2).

TABLE 2. ELECTRON MICROPROBE ANALYSES OF CABRIITE

	Pd	Pt	Sn	Cu	Ag	Sb	Σ	Formula
1	55.5	-	27.5	16.0	-	2.2	101.2	$Pd_{2.04}(Sn_{0.91}Sb_{0.07})_{0.98}Cu_{0.98}$
2	51.0	1.0	30.0	16.0	2.0	1.0	101.0	$(Pd_{1.89}Pt_{0.02}Ag_{0.07})_{1.98}(Sn_{1.00}Sb_{0.03})_{1.03}Cu_{0.99}$
3	51.4	3.3	28.0	12.7	0.5	1.4	97.3	$(Pd_{2.03}Pt_{0.07}Ag_{0.02})_{2.12}(Sn_{0.99}Sb_{0.05})_{1.04}Cu_{0.84}$
4	49.5	7.1	29.2	15.2	-	-	101.0	$(Pd_{1.88}Pt_{0.15})_{2.03}Sn_{1.00}Cu_{0.97}$
5	53.5	3.7	29.5	15.3	-	-	102.0	$(Pd_{1.99}Pt_{0.08})_{2.07}Sn_{0.98}Cu_{0.95}$
6	52.1	2.6	30.0	16.2	-	-	100.9	$(Pd_{1.94}Pt_{0.05})_{1.99}Sn_{1.00}Cu_{1.01}$
7	52.05	-	30.11	17.28	-	-	99.44	$Pd_{1.93}Sn_{1.00}Cu_{1.07}$
8	53.98	-	29.45	15.21	-	-	98.64	$Pd_{2.04}Sn_{1.00}Cu_{0.96}$

Note: No. 1 by I.D. Marchukova (MS-46, IMET AN SSSR), No. 2 by Yu. E. Ugaste (MS-46, IMET AN SSSR), No. 3 by N.V. Troneva (MAR-1, GIREDMET), No. 4 by V.S. Malov (MS-46, IGEM AN SSSR), No. 5 by I.P. Laputina (MS-46, IGEM AN SSSR), No. 6 by J.H.G. Laflamme (MAC-400, CANMET), Nos. 7, 8 (CAMEBAX, IFZ AN SSSR).

TABLE 3. X-RAY POWDER DATA FOR CABRIITE, SYNTHETIC Pd_2SnCu AND Pd_3Sn

Cabriite		hkl	dÅ calc.	Pd_2SnCu synthetic		Pd_3Sn (cubic, Pm3m, a = 3.88Å)		
I	dÅ meas.			I	dÅ meas.	I	dÅ meas.	hkl
0.5	2.51	130	2.49	-	-	-	-	-
10	2.29	221	2.28	8	2.28	10	2.25	111
9	2.17	230, 301	2.19	10	2.19	-	-	-
1	2.10	131	2.10	-	-	-	-	-
0.5	1.962	400, 002	1.970	0.5b	1.965	6	1.943	200
-	-	102, 231, 140	1.911	0.5b	1.918	-	-	-
3b	1.840	330, 112	1.858	2b	1.838	-	-	-
0.5b	1.780	240, 202	1.762	-	-	1	1.758	210
1b	1.601	222, 241	1.609	2b	1.617	-	-	-
-	-	-	-	0.5b	1.481	-	-	-
3b	1.434	151	1.439	1	1.435	-	-	-
-	-	440, 402	1.393	1b	1.397	6	1.376	220
1	1.367	251, 142	1.372	-	-	-	-	-
-	-	332, 350	1.351	1b	1.345	-	-	-
1b	1.291	160, 103	1.296	2b	1.290	1	1.293	221, 300
8	1.230	161, 450, 502,	1.231	5	1.233	-	-	-
-	-	342, 123						
4	1.217	152	1.216	1	1.218	-	-	-
3	1.182	223, 261	1.188	1	1.184	10	1.175	311
-	-	442	1.138	1	1.137	4	1.124	222
0.5b	1.118	170, 550	1.115	-	-			
2b	1.094	602, 403	1.093	2b	1.090			
1b	1.083	270, 701, 143	1.083	-	-			
-	-	171, 333, 551	1.073	1	1.073			
0.5	1.037	370	1.035	0.5	1.035			
-	-	343, 560, 503	1.011	0.5	1.011			

Note: b - broad line. Intensities were estimated by eye; Fe-radiation (- lines were determined by calculation). Powder patterns on a monocrystal grains with 57.3 mm Gandolfi camera. The compositions of cabriite - anal. no. 4 and Pd_2SnCu - anal. no. 8 (Table 2).

A minimum of ten spots were analyzed for each grain, and variations of element line-intensities in homogeneous grains did not exceed 2%. Relative intensities were transformed into weight concentrations by the ZAF correction procedure. The standard deviation of the intensity ratios was 10% relative (for small concentrations) at the worst and 3–5% relative on average. Compositions 1, 4 and 5 (Table 2) were calculated with the Springer algorithm (Springer 1967). Absorption corrections were applied according to Philibert (1964) and Duncumb & Reed (1968) for atomic number. Compositions 2 and 3 (Table 2) were recalculated using the formulae of Rydnik & Borovskii (1967) and the absorption factors of Heinrich (1966).

Table 2 also presents the composition of a cabriite specimen, kindly provided by L.J. Cabri. It was obtained using an MAC–400 probe with reference to synthetic $(Pd_{4.85}Cu_{0.15})_5Sb_2$ for Pd$L\alpha_1$, synthetic PtSn for Pt$L\alpha_1$ and Sn$L\alpha_1$ and pure copper for Cu$K\alpha_1$. Raw data were processed with the MAGIC IV computer program by J.W. Colby (Bell Telephone Laboratories Inc., Allentown, Pa.).

Analyses of synthetic Pd_2SnCu (7 and 8, Table 2) were obtained on a CAMEBAX microprobe operated at 30 kV and 20 nA, using stoichiometric Pd_2Sn and pure copper as standards for 10–20 s counting times. These analytical data were processed using the CARAT computer program of Berdichevskii *et al.* (1977). It is noteworthy that several cabriite grains contain platinum, up to 7.1 wt.% in sample 4. Generally, the composition is always close to $(Pd,Pt)_2SnCu$.

Though grains of cabriite are relatively large (up to 0.2 mm), it was rather difficult to obtain a good X-ray powder pattern of the mineral. Like all Pd–Sn–Cu minerals, cabriite is very ductile. Thus, an X-ray powder photograph of a sample of powder-size grains rolled in a rubber ball gave only 3 or 4 smeared lines. However, a sufficiently detailed pattern was obtained using a 57.3-mm Gandolfi camera and Fe radiation, which permitted easy comparison with X-ray patterns of synthetic Pd_2SnCu and Pd_3Sn (Table 3).

Discussion of the Structure

Determination of the unit cell and structure of cabriite and its synthetic analogue by single-crystal methods was not possible because the grains consist of finely twinned aggregates (Fig. 2). We therefore examined data on the behavior of phases in the pseudobinary system Pd_3Sn–Cu_3Sn in the temperature range from 25 to 1000°C for clues on the structural characteristics of cabriite on the X-ray powder patterns. Evstigneeva & Nekrasov (1980) have studied the high-temperature phase relations in part of the system Pd_3Sn–Cu_3Sn (0–60 mol.% Cu_3Sn) and found an extensive field of solid solution of the Cu_3Au structure-type (Fig. 3). At lower

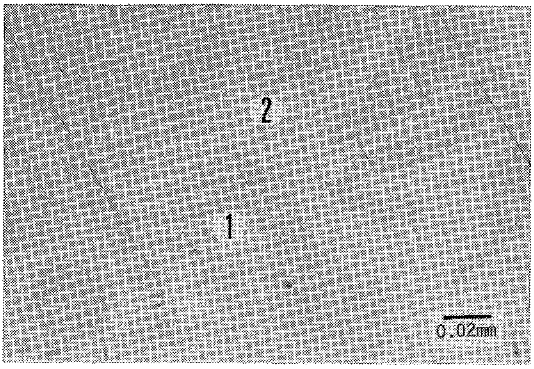


FIG. 2. Twin structure of Pd_2SnCu (1) intergrown with Pd_2Sn (2). Partly crossed nicols.

temperatures, the Pd–Sn–Cu phases exhibit a lowering of symmetry due to the ordering of Pd and Cu atoms in their respective cubic structures.

This change in symmetry was directly observed by use of high-temperature X-ray diffraction. The cubic solid-solution $(Pd,Cu)_3Sn$ with 16.2 wt.% Cu changes to ordered Pd_2SnCu at 200°C (Fig. 4). This ordering process is very characteristic of metallic compounds.

Possible variants of the Pd_2SnCu structure may be proposed, as listed in Table 4; the most likely is thought to be no. 5. (F^2_{exp} values were calculated roughly according to the observed intensities of the X-ray powder pattern; comparison of these data with F^2_{calc} gave the best correspondence with no. 5.)

Thus the X-ray pattern of synthetic Pd_2SnCu and cabriite are indexed in an orthorhombic elementary cell (*Pmmm*, $Z = 4$) with $a \simeq b \simeq 7.88(5)$, $c \simeq 3.94(2)$ Å. The calculated density for cabriite (sample 4, Table 2) is 11.1 g/cm^3; it is 10.7 g/cm^3 for the ideal composition Pd_2SnCu.

MINERAL ASSEMBLAGES AND CONDITIONS OF FORMATION

Cabriite is characteristically found in massive copper-nickel sulfide ores composed mainly of metal-rich minerals of the chalcopyrite group, such as mooihoekite $Cu_9Fe_9S_{16}$, putoranite $Cu_{18}(Fe,Ni)_{18}S_{32}$ and talnakhite $Cu_{18}(Fe,Ni)_{16}S_{32}$. The mineral usually occurs as individual grains up to 200 μm in size (Fig. 5), but it is sometimes closely intergrown with polarite, sobolevskite [putoranite ore], sperrylite (Fig. 6) and other platinum-group minerals.

Cassiterite and stannite also occur in association with cabriite and other Pd–Sn–Cu minerals in galena–chalcopyrite vein ores (Fig. 7a, b). Textural relations of cassiterite and cabriite suggest that they were formed contemporaneously. This mode of formation is in agreement with the synthesis experiments of Pd–Sn and Pd–Sn–Cu compounds from Cl-bearing solutions at temperatures below 500°C and a pressure of 1 kbar (Evstigneeva *et al.* 1979, Evstigneeva & Nekrasov 1980). In these experiments, cassiterite was commonly found with cabriite and other Pd–Sn–Cu phases. Stannite also occurs be-

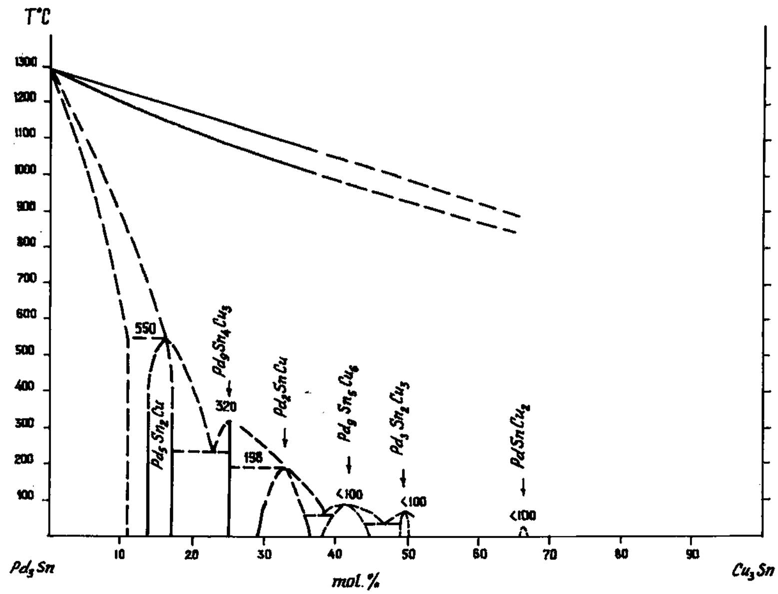


FIG. 3. Subsolidus phase diagram for part of the system Pd_3Sn–Cu_3Sn (Evstigneeva & Nekrasov 1980).

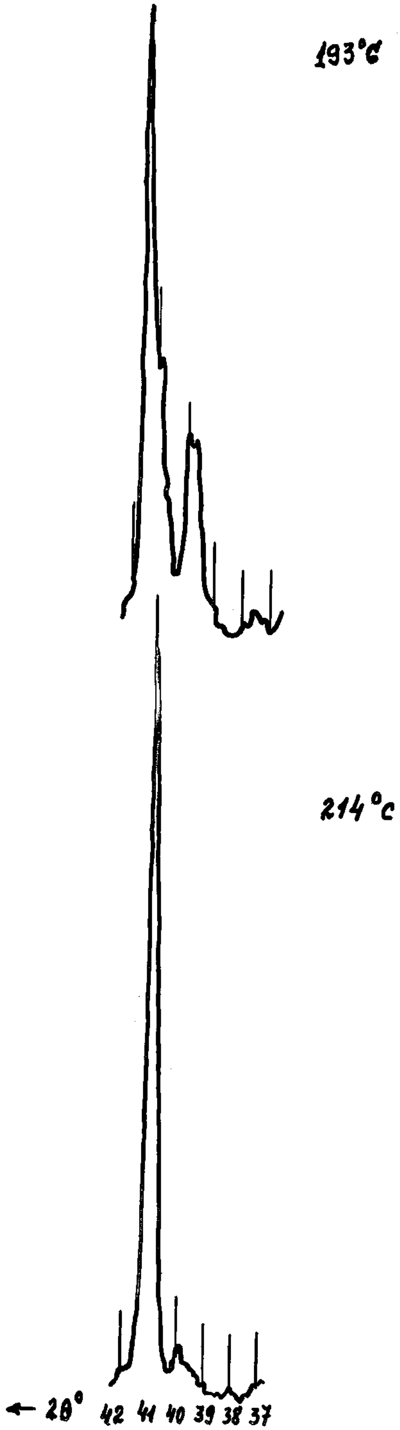


FIG. 4. Structural transformations in Pd–Sn–Cu phase containing ~16.2% Cu; a) cubic $(Pd,Cu)_3Sn$, a 3.89 Å, T = 214°C, the (111) peak; b) orthorhombic Pd_2SnCu, $a \cong b \cong 7.88$, $c \cong 3.94$ Å, T = 190°C, the (230,301) and (221) peaks.

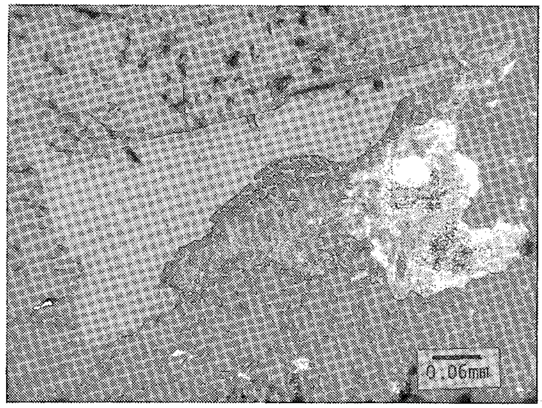


FIG. 5. Cabriite (white) inclusion in talnakhite (grey) and cubanite (dark grey). Magnetite appears black.

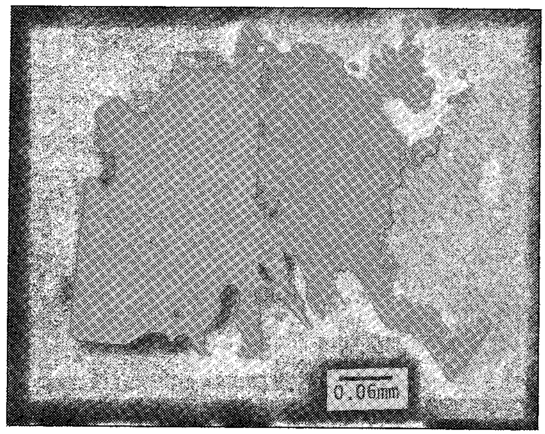


FIG. 6. Intergrowth of cabriite (grey) and sperrylite (white) in bornite ore from the exocontact.

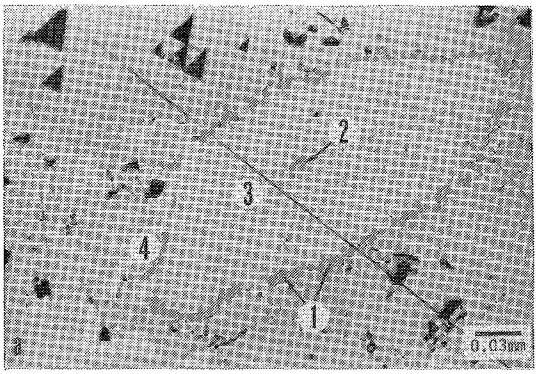
tween the platinum-group minerals and the ore-forming sulfides and probably formed as a reaction rim. It should also be mentioned that Distler & Laputina (1980) made suggestions on the formation of cassiterite (followed by stannite) after crystallization of intermetallic compounds of palladium in "a comparatively dry system at higher temperatures". Such suggestions, however, require confirmation.

NOMENCLATURE AND PRESERVATION OF TYPE MATERIAL

The name *cabriite* and the mineral Pd_2SnCu have been approved by the Commission on New Minerals and Mineral Names (I.M.A.). The name honors Dr. L.J. Cabri, famous Canadian mineralogist, who was the first to discover a great number of platinum-group minerals and who made important contributions to the mineralogy and geochemistry of this

TABLE 4. POSSIBLE VARIANTS OF Pd_2SnCu STRUCTURE

No.	Space Group	Unit cell *a*	Unit cell *b*	Unit cell *c*	Atom positions Pd	Atom positions Sn	Atom positions Cu	Z
1	*Pmmm*	4x3.94	3x3.94	3.94	2(1/8 0 ½); 2(0 1/6 ½); 4(¼ 1/6 ½); 4(1/8 1/3 ½); 4(3/8 1/3 ½); 2(1/8 ½ 0); 2(3/8 ½ 0); 4(3/8 1/6 0);	1(000); 1(½ 00); 2(½ 2/3 0); 2(¼ 00); 2(0 1/3 0); 4(¼ 1/3 0);	4(1/8 1/6 0); 1(0 ½ ½); 2(½ 1/6 ½); 1(½ ½ ½); 2(3/8 - ½); 2(¼ ½ ½);	12
2	*P4/mmm*	3.94	3.94	3.94	2(½ 00)	1(000)	1(½ ½ 0)	1
3	*P4/mmm*	2x3.94	2x3.94	3.94	4(¼ ¼ 0); 4(½ ¼ ½)	1(000); 2(½ 00); 1(½ ½ 0)	4(¼ 0 ½)	4
4	*Pmma*	2x3.94	3.94	2x3.94	2(¼ ½ ½); 2(¼ 0 ¼) 4(0 ½ ¼)	2(000); 2(00 ½)	2(¼ 0 ¾); 2(¼ ½ 0)	4
5	*Pmmm*	2x3.94	2x3.94	3.94	1(½ 00); 1(0 ½ 0); 2(0 ¼ ½); 2(½ ¼ ½); 2(¼ 0 ½)	4(¼ ¼ 0)	1(000); 1(½ ½ 0); 2(¼ ½ ½)	
6	*P4mm*	3.94	3.94	2x3.94	1(½ ½ ½); 2(0 ½ ¼); 1(½ ½ 0);	1(000); 1(00 ½)	2(0 ½ ¾)	



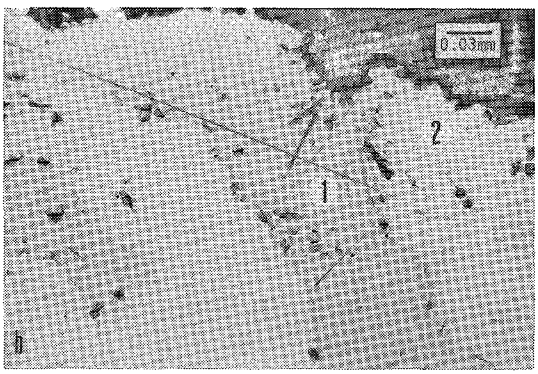


FIG. 7. a) Stannite (1) and cassiterite (2) intergrown with Pd_2Sn (3) and $PdBi_2$ (4) in galena–chalcopyrite vein ore. b) Cassiterite needles in cabriite (1) with paolovite (2). Galena–chalcopyrite vein ore.

group. Polished sections with cabriite are preserved in the Mineralogical Museum of the Academy of Sciences of the USSR, in the Mineragraphy Laboratory of IGEM, Academy of Sciences of the USSR, both in Moscow and in the National Mineral Collection, Geological Survey of Canada, Ottawa.

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