Tatyanaite, a new platinum-group mineral, the Pt analogue of taimyrite, from the Noril'sk complex (northern Siberia, Russia)

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Tatyanaite, a new platinum-group mineral, the Pt analogue of taimyrite, from the Noril'sk complex (northern Siberia, Russia)

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Abstract: Tatyanaite, a new mineral from Noril'sk (Siberia), is the Pt analogue of taimyrite. It is defined as the member(s) of the tatyanaite-taimyrite solid-solution series with Pt > Pd. Tatyanaite solid solution occurs in massive sulphide ore, which consists of chalcopyrite and subordinate pentlandite, pyrrhotite, and cubanite (or isocubanite). It occurs as central zones of large, elongate grains (up to ~1 mm) and as aggregates of smaller grains associated with Ag-Au alloys. The associated minerals include unusually Pt-rich taimyrite [$(Pd_{1.25}Pt_{0.86})(Cu_{0.85}Ni_{<0.01})(Sn_{1.01}Sb_{0.02})$], atokite-rustenburgite, paolovite, froodite, sperrylite, maslovite, and galena. Cryptic zoning (Pt increases and Pd decreases toward the centre) and polysynthetic twins are characteristic. In reflected light, tatyanaite is pink with lilac tinge in air. Bireflectance is weak to distinct, from brownish pink to pinkish lilac. Anisotropy is distinct to moderate, from light brown to dark blue. Reflectance percentages in air and (in oil) are, for R_1 and R_2, 470 nm 42.8, 44.1 (32.8, 33.3), 546 nm 49.5, 50.0 (37.6, 38.8), 589 nm 51.8, 54.6 (38.9, 39.9), and 650 nm 55.6, 56.8 (41.6, 44.2). It is ductile; the microhardness is VHN_{20} = 292-348, mean of 327 kg/mm^2. The average of nine electron-microprobe analyses gave Pt 45.38, Pd 19.53, Cu 10.62, Ni 0.15, Fe 0.03, Sn 23.02, Sb 0.27, sum 99.0 wt.%, corresponding to $[(Pt_{4.76}Pd_{3.75})_{\Sigma 8.51}Cu_{0.48}]_{\Sigma 8.99}(Cu_{2.94}Ni_{0.05}Fe_{0.01})_{\Sigma 3.00}(Sn_{3.96}Sb_{0.05})_{\Sigma 4.01}$ [or to $(Pt_{1.19}Pd_{0.94})(Cu_{0.85}Ni_{0.01}Fe_{<0.01})$ $(Sn_{0.99}Sb_{0.01})$]. The powder pattern is similar to that of synthetic $Pd_9Cu_3Sn_4$, and, by analogy with the latter, it was indexed for an orthorhombic cell with a = 7.89(1) Å, b = 4.07(1) Å and c = 7.73(1) Å, and V = 248(1) Å^3. The three strongest lines in the pattern are 2.283 (10, 212), 2.163 (4, 203) and 1.369 (3, 323). Tatyanaite-taimyrite formed from a late-stage liquid rich in noble metals, Cu and Sn.

Key-words: tatyanaite, taimyrite, new mineral, platinum-group mineral, platinum-group elements, tin, Cu-Ni sulphide ores, Oktyabr'sky deposit, Noril'sk complex, Siberia, Russia.

Introduction

Deposits of the platinum-group elements of the Noril'sk complex of Siberia, Russia, contain various Pd-(Pt)-Cu-Sn-(Sb) minerals, *i.e.*, taimyrite, cabriite and stannopalladinite, which are exceptionally rare in other complexes. Typically, these platinum-group minerals (*PGM*) display low

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to moderate levels of Pt: up to ~15 wt.% Pt in taimyrite, up to ~7 wt.% Pt in cabriite and up to 1 wt.% Pt in stannopalladinite (Genkin *et al.*, 1981; Begizov *et al.*, 1982; Evstigneeva & Genkin, 1983). In this paper, we report on the existence of a new species of *PGM*, tatyanaite, which is the Pt-dominant analogue of taimyrite; it is associated with unusually Pt-rich taimyrite (~ 35 wt.% Pt). Tatyanaite has been found in a specimen of sulphide ore from the Oktyabr'sky deposit, Noril'sk, and is named after Dr. Tatyana L. Evstigneeva (or Yevstigneeva; b. 1945) of the Russian Academy of Sciences (IGEM, Moscow), who has been involved for many years in research on *PGM* and various ore minerals of the Noril'sk complex. The new mineral and its name have been approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association. A sample of the tatyanaite solid solution from the type locality is preserved in the Museum at the University of Hamburg, Germany.

Occurrence

Tatyanaite occurs in massive sulphide ore from the Oktyabr'sky deposit. The principal base-metal sulphide is chalcopyrite and, possibly, a chalcopyrite-like sulphide (*e.g.*, mooihoekite, talnakhite or putoranite). Subordinate pentlandite and pyrrhotite, and minor galena also are present in the ore. The gangue minerals are unidentified Fe-rich hydrous silicate, accessory magnetite and calcite. Commonly, the *PGM* occur as composite veinlet-like and irregular grains up to ~ 1 mm in length. Individual grains of smaller size also are present. The *PGM* in the association are members of the atokite (Pd_3Sn) – rustenburgite (Pt_3Sn) solid-solution series, paolovite (Pd_2Sn), froodite ($PdBi_2$), sperrylite ($PtAs_2$), rare maslovite (PtBiTe), and unnamed $Pd_2(Sn,Sb)$. Many of these minerals typically are associated with grains of Ag-Au alloy. A small (≤ 20 µm) grain of a Cl-rich (~ 3 wt.% Cl) ferropyrosmalite was also found in this sample.

Tatyanaite occurs as central zones of large elongate grains (up to ~ 1 cm in the longest dimension) and as aggregates of smaller, irregular or platy grains. They are most closely associated with chalcopyrite, atokite-rustenburgite and Ag-Au alloy (*e.g.*, Fig. 1). Typically, the grains are cryptically zoned with respect to Pt and Pd: platinum is most enriched in the core, whereas the content of Pd increases toward the rim. Thus

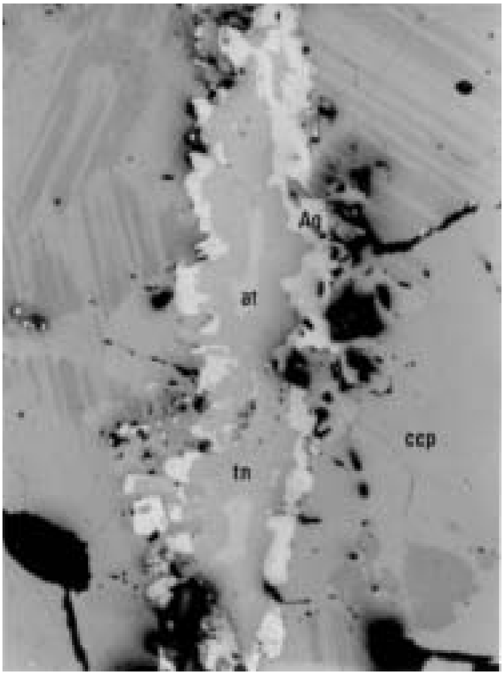

Fig. 1. A grain of tatyanaite-(Pt-rich)- taimyrite, tn, from the massive sulphide ore of the Oktyabr'sky ore deposit, Noril'sk. The grain contains two elongate inclusions of atokite-rustenburgite (at) in the centre and is mantled by a rim-like Ag-Au alloy (Ag). The host is chalcopyrite (ccp) with lamellae of cubanite or isocubanite. Reflected-light photomicrograph. The grain is 0.8 mm in length.

tatyanaite and atokite-rustenburgite are found closer to the centre of grains, and Pt-rich taimyrite is found closer to the edge of the zoned grains. The Ag-Au alloy is strongly variable in composition; for instance, the grains in Fig. 1 display the ranges $Ag_{0.53-0.89}Au_{0.47-0.11}$.

Optical properties and microhardness

In reflected light, tatyanaite is pink with lilac tinge. Bireflectance is weak to distinct, and reflection pleochroism is from brownish pink to pinkish lilac. The anisotropy is distinct to moderate, from light brown to dark blue. The grains exhibit a peculiar shred-like or mosaic-like texture, and polysynthetic twins are present. No cleavage or internal reflections were observed. Reflectance measurements were carried out on a randomly oriented, weakly bireflectant grain. The spectra of

Table 1. Reflectance data for tatyanaite.

λ nm	R_1% (air)	R_2% (air)	R_1% (oil)	R_2% (oil)
400	40.6	41.5	30.7	31.2
420	41.1	42.1	31.0	31.6
440	41.7	42.6	31.5	32.0
460	42.0	43.5	32.4	32.9
470	42.8	44.1	32.8	33.3
480	43.1	45.0	33.7	34.1
500	45.3	46.8	34.9	35.9
520	47.0	48.1	36.8	37.3
540	49.1	49.6	37.2	38.1
546	49.5	50.0	37.6	38.8
560	51.0	51.8	38.2	39.1
580	51.5	53.9	38.4	39.5
589	51.8	54.6	38.9	39.9
600	52.8	55.0	40.3	41.5
620	54.5	55.8	40.5	42.8
640	55.0	56.2	40.9	43.6
650	55.6	56.8	41.6	44.2
660	56.5	57.3	41.8	44.5
680	57.2	57.8	43.5	46.1
700	57.7	58.1	44.3	47.9

Spectra obtained with a Zeiss MPM spectrophotometer. Reflectance standard used: WTiC (R_{589} in air 49.5 %).

tatyanaite (Table 1, Fig. 2) are similar to those of taimyrite from the type occurrence (Begizov *et al.*, 1982). The colour values are given in Table 2. The mineral is rather ductile. Microhardness values of tatyanaite are VHN_{20} = 292-348 (six indentations), mean of 327, and they correspond to a Mohs hardness of ~ $3^1/_2$-4. These values are lower than those reported by Begizov *et al.* (1982) for their sample of taimyrite (VHN_{50} = 480 ± 25), but they are in agreement with the values $VHN_{5,10,20,50,100}$ between 251 and 344, which were obtained for an unnamed taimyrite-like phase from Noril'sk (Razin *et al.*, 1976). Microhardness values of cabriite also are similar: VHN_{50} in the range 258-282, mean 272 (Evstigneeva & Genkin, 1983).

Table 2. Colour values for tatyanaite (C illuminant).

		x	Y	Y%	P_e%	λ_d
in air	R_1	0.331	0.335	50.0	10.6	579
in air	R_2	0.332	0.334	51.3	10.5	580
in oil	R_1	0.329	0.334	37.9	9.8	578
in oil	R_2	0.331	0.335	38.9	10.7	580

Reflectance percentages in air and in oil are given in Table 1.

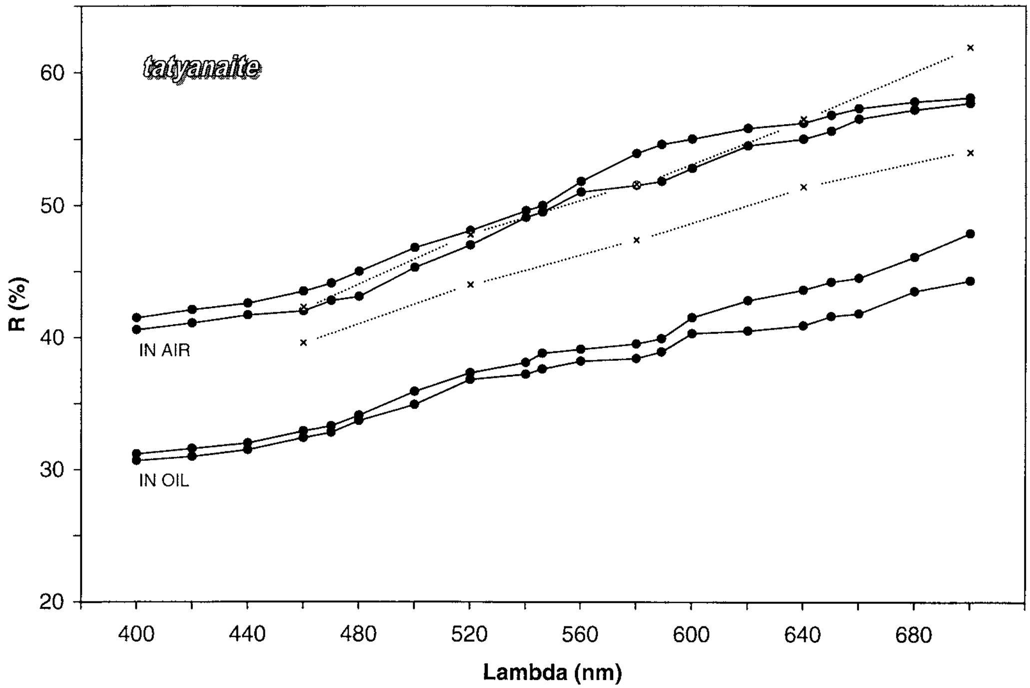

Fig. 2. Comparison of reflectance data for tatyanaite (filled circles) and taimyrite from the type locality (dashed line; after Begizov *et al.*, 1982). The reflectance was measured in air and in oil; values (*R* %) are plotted *versus* wavelength λ in nm.

Table 3. Representative results of electron microprobe analyses for tatyanaite and associated Pt-rich taimyrite from the Noril'sk complex, Siberia.

	Tatyanaite				Pt-rich taimyrite		
	Average (n = 9)	Range*	Average (n = 3)	Range**	Average (n = 30)	Range*	n = 1
No.	*1**		*2***		*3**		*4***
Pt	45.38	41.9-48.04	45.01	42.45-46.81	34.92	31.37-40.19	35.35
Pd	19.53	16.63-21.83	19.61	18.41-21.35	27.77	23.67-30.95	27.16
Cu	10.62	9.59-11.35	10.53	10.36-10.84	11.33	10.04-11.79	11.28
Fe	0.03	0.0-0.09	n.a.	--	0.04	0.0-0.40	n.a.
Ni	0.15	0.12-0.20	0.10	0.08-0.12	0.09	0.02-0.37	0.08
Sn	23.02	22.11-24.03	22.80	22.57-23.27	24.95	23.49-25.65	24.59
Sb	0.27	0.09-0.49	n.a.	--	0.46	0.05-1.19	n.a.
Pb	n.d.	0.0-0.13	n.a.	--	n.d.	0.0-0.21	n.a.
Total	99.00		98.05		99.56		98.46

Note: wavelength-dispersion electron microprobe analyses (wt.%). *n:* number of individual analyses. n.a.: not analysed, n.d.: not detected. Bi, Te and S were sought, but not detected. * JEOL-8900 electron microprobe (McGill University). ** Cameca-Camebax electron microprobe (University of Hamburg).

Chemical composition and formula

Two sets of wavelength-dispersion electron-microprobe analyses of tatyanaite were obtained. A JEOL JXA-8900 electron microprobe (McGill University) was operated at an accelerating voltage of 20 kV and a probe current of 20 nA. X-ray lines and (standards) used were Pt*L*α ($PtAs_2$), Pd*L*α (Pd_3HgTe_3), Cu*K*α (chalcopyrite), Ni*K*α (pentlandite), Fe*K*α (pyrite), Sn*L*α (SnO_2), Sb*L*α (stibnite) and Pb*L*α (PbS). Except for the tin dioxide, all these standards were supplied by CANMET, Ottawa, Canada. The standard Pd_3HgTe_3 was reanalysed using a metallic Pd standard, and its Pd concentration was confirmed. A Cameca-Camebax electron microprobe (University of Hamburg) was operated at an accelerating voltage of 20 kV and a probe current of 23 nA. X-ray lines and (standards) used were Pt*L*α, Pd*L*α, Cu*K*α, Ni*K*α, (pure metals), Sn*L*α (SnO_2), Te*L*α and Bi*M*α (PdBiTe).

Average results of the electron-microprobe analyses are in excellent agreement with each other (Tables 3 and 4). Platinum, Pd, Cu and Sn are the main constituents; Ni, Fe, Sb and Pb are minor or present at trace levels. As in the case for the associated Pt-rich taimyrite (anal. 3 and 4, Tables 3 and 4) and the taimyrite from the type locality (Begizov *et al.*, 1982), the atomic (Pt + Pd + Cu) : Sn ratiob of tatyanaite is 3:1. The content of Pt and Pd varies strikingly; these elements exhibit a perfect inverse correlation (correlation coefficient: -1.00). In contrast, the Cu concentration of tatyanaite and coexisting Pt-rich taimyrite is

Table 4. Atomic proportions of tatyanaite and associated Pt-rich taimyrite.

	Tatyanaite				Pt-rich taimyrite			
Analysis no.	*1* *	*1* *	*2* **	*2* **	*3* *	*3* *	*4* **	*4* **
Σ atoms	*16*	*4*	*16*	*4*	*16*	*4*	*16*	*4*
Pt	4.76	1.19	4.77	1.19	3.43	0.86	3.53	0.88
Pd	3.75	0.94	3.81	0.95	5.00	1.25	4.97	1.24
Cu	3.42	0.85	3.42	0.86	3.42	0.85	3.45	0.86
Fe	0.01	<0.01	--	--	0.01	<0.01	--	--
Ni	0.05	0.01	0.04	0.01	0.03	<0.01	0.03	<0.01
Σ	11.99	2.99	12.04	3.01	11.89	2.97	11.98	2.99
Sn	3.96	0.99	3.97	0.99	4.03	1.01	4.03	1.01
Sb	0.05	0.01	--	--	0.07	0.02	--	--
Pb	--	--	--	--	--	--	--	--
Σ	4.01	1.00	3.97	0.99	4.10	1.03	4.03	1.01

Note: the electron microprobe data (in wt.%) are listed in Table 3. * JEOL-8900 electron microprobe (McGill University). **Cameca-Camebax electron microprobe (University of Hamburg).

invariant (*cf.* anal. 1 and 3, Tables 3 and 4). We surmise that there is a separate site occupied by Cu in the structure, as in the case of another Pd-Cu-Sn-rich *PGM*, oulankaite [$(Pd,Pt)_5(Cu,Fe, Ag)_4SnTe_2S_2$] (Barkov *et al.*, 1996). This possibility is consistent with the version of the ideal formula of taimyrite, $Pd_9Cu_3Sn_4$, suggested by Evstigneeva & Nekrasov (1984) as an alternative to the formula $(Pd,Cu,Pt)_3Sn$ of Begizov *et al.* (1982). Our analytical data for the taimyrite-tatyanaite series from Noril'sk (Barkov *et al.*, 2000) suggest the presence of limited Cu-Pd substitution in this series. The existence of a separate Cu site, however, is not inconsistent with these results. If calculated on the basis of Σ atoms = 16, the content of Sn in the empirical formulae of tatyanaite (Table 4) is 4 atoms per formula unit. Other possible variants, such as $(Pt,Pd)_{2+x}Cu_{1-x}Sn$ and $(Pt,Pd)_{17}Cu_7Sn_8$ [or $(Pt,Pd)_{15}Cu_6Sn_7$], also were taken into account, but the general formula $(Pt,Pd,Cu)_9Cu_3Sn_4$ is preferred at this stage, because of the similarity in atomic proportions and X-ray data between tatyanaite and the synthetic taimyrite, $Pd_9Cu_3Sn_4$.

X-ray powder-diffraction data

Owing to the presence of twins and the zoning, no single-crystal study of tatyanaite could be undertaken; it was characterised instead by X-ray powder diffraction. After electron-microprobe analysis, the powder was extracted by micropicking and studied with a 57.3 mm Debye-Scherrer camera, Fe*K*α radiation. The pattern obtained (Table 5) displays similarities with those of synthetic taimyrite (Evstigneeva & Nekrasov, 1984) and the taimyrite from Noril'sk (Begizov *et al.*, 1982). However, the line having a $d_{obs.}$ of 2.36 Å (I = 3 to 5) reported by Begizov *et al.* (1982) is absent in the tatyanaite (and synthetic taimyrite) patterns (Table 5). In

Table 5. Comparison of X-ray powder data for tatyanaite and taimyrite.

Tatyanaite				Taimyrite*		Taimyrite**		Synthetic $Pd_9Cu_3Sn_4$§		
I	d *meas.*	d *calc.*	hkl	I	d *meas.*	I	d *meas*	I	d *meas.*	hkl
						½	3.64			
						½	3.36			
1	2.805	2.802	012	1	2.82					
								10	2.64	112, 300
1	2.439	2.450	103					5	2.51	103
						5	2.36			
10	2.283	2.285	212	10	2.28	6	2.29	100	2.27	212
								10	2.21	312, 213
4	2.163	2.158	203	4	2.16	10	2.16	100	2.17	203, 310
1	2.100	2.099	113							
2	2.030	2.034	020	3	2.03	2	2.04			
						½	1.942	10	1.955	400, 200
						½	1.913			
1	1.870	1.877	104	1	1.878			5	1.843	303, 112
						½	1.718			
1	1.630	1.638	222			1	1.633	10	1.610	222, 214
1	1.440	1.440	205	1	1.446	4	1.443	10	1.458	205, 223
						1	1.372	10	1.393	404, 420
3	1.369	1.365	323	2	1.358	1	1.354	60	1.348	305, 323
						½	1.343	60	1.291	106, 130
1	1.263	1.267	315			3	1.302	10	1.273	315, 131
		1.265	231							
		1.263	132							
1	1.228	1.228	016			3	1.227	10	1.250	206, 610
2	1.218	1.217	405, 232	3	1.213			70	1.229	324, 405, 132
						1	1.178	20	1.172	330, 315, 415
						2	1.166			
2	1.143	1.142	424			1	1.140	60	1.140	424
1	1.128	1.128	700	1	1.132			30	1.131	700, 233
						1	1.095			
1	1.082	1.083	702			1	1.081	60	1.084	207, 134
						1	1.018			

* Taimyrite from Noril'sk (this study); sample courtesy of V.D. Begizov & V.N. Yakovenchuk. Values of d are reported in Å.

** Taimyrite after Begizov *et al.* (1982). *a* = 16.11 Å, *b* = 11.27 Å and *c* = 8.64 Å (or *a* = 12.57 Å, *b* = 13.40 Å and *c* = 17.09 Å).

§ Synthetic taimyrite after Evstigneeva & Nekrasov (1984). *a* = *c* = 7.88 Å and *b* = 3.89 Å.

order to clarify this situation, a grain of taimyrite from the type locality (supplied by V.N. Yakovenchuk & V.D. Begizov) was examined using the same experimental conditions. This line was not observed in the new pattern of the taimyrite (Table 5). An admixture of Au-(Ag) alloy may be responsible for this line in the previous study. Many lines in the tatyanaite pattern are broad and diffuse, as in the case in other Pd-Cu-Sn intermetallic compounds (*e.g.*, Razin *et al.*, 1976; Evstigneeva & Nekrasov, 1984). The similarities between the patterns of tatyanaite and taimyrite (both natural and synthetic) suggest that they are isostructural. The difference in intensities (Table 5) may result, at least in part, from different facilities and experimental conditions used. By analogy with synthetic taimyrite ($Pd_9Cu_3Sn_4$), the X-ray powder pattern of tatyanaite was indexed on the basis of an orthorhombic cell with the parameters a = 7.89(1) Å, b = 4.07(1) Å and c = 7.73(1) Å, V = 248(1) Å^3. A single-crystal study is, however, needed to check the cell parameters calculated from the powder-diffraction data. Probable space-groups, also by analogy with the synthetic material, are *Pmmm*, *Pmm*2 or *P*222. With Z = 1, the density calculated using the average composition (anal. 1, Tables 3 and 4) is 13.55 g/cm^3.

Related intermetallic compounds

Tatyanaite is most closely related to taimyrite (Begizov *et al.*, 1982), which has the average composition $(Pd_{2.12}Pt_{0.26}Cu_{0.64})_{\Sigma 3.02}(Sn_{0.85}Sb_{0.12}Pb_{0.01})_{\Sigma 0.98}$ (n = 6); the relative enrichment in Cu in tatyanaite implies a solid solution toward cabriite, Pd_2CuSn. It is also related to the unnamed analogue of taimyrite, of average composition $(Pd_{2.09}Pt_{0.25}Cu_{0.72})_{\Sigma 3.06}Sn_{0.94}$, which is orthorhombic according to an electron-microdiffraction study (Razin *et al.*, 1976). All of these related intermetallic compounds occur in the Noril'sk complex.

In the system Pd_3Sn - Cu_3Sn, Evstigneeva & Nekrasov (1984) reported evidence for six ternary compounds, which form as a result of solid-state transformations over a temperature interval from 550 to ~ 100°C, with an increasing Cu concentration of these phases. According to these authors, three of these phases, the ones richest in Pd, Pd_5CuSn_2 [or $(Pd_{2.5}Cu_{0.5})_{\Sigma 3.0}Sn$], $Pd_9Cu_3Sn_4$ [$Pd_{2.25}Cu_{0.75})_{\Sigma 3.0}Sn$] and Pd_2CuSn, represent synthetic equivalents of the minerals stannopalladinite, taimyrite and cabriite, respectively. These three *PGM* are rather similar in composition and also in optical and physical properties. They commonly are polysynthetically twinned and yield similar X-ray powder patterns, which are suggestive of orthorhombic symmetry (Evstigneeva & Nekrasov, 1984). Studies involving precession methods are needed to better understand the relationships among these *PGM.*

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