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THE TAIMYRITE–TATYANAITE SERIES AND ZONING IN INTERMETALLIC COMPOUNDS OF Pt, Pd, Cu, AND Sn FROM NORIL'SK, SIBERIA, RUSSIA

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ABSTRACT

We report on the existence of a newly recognized extensive solid-solution series between taimyrite and tatyanaite, its Pt-dominant analogue. Copper probably occupies a separate site. Substitution involving Pd and Cu also is important, such that taimyrite–tatyanaite forms a solid-solution series with cabriite, which is structurally closely related to taimyrite and tatyanaite. These platinum-group minerals (*PGM*) occur in base-metal sulfide (*BMS*) ores in the Oktyabr'sky deposit, Noril'sk complex, Siberia, Russia. The taimyrite–tatyanaite is present as single grains and aggregates, associated with a heterogeneous Ag–Au alloy, and also as zoned intergrowths of Pt–Pd–Cu stannides. These intergrowths commonly, but not necessarily, occur within chalcopyrite and typically display the following sequence of crystallization, based on textural and compositional data: atokite–rustenburgite → tatyanaite → Pt-rich taimyrite → taimyrite poorer in Pt → late-stage Ag–Au alloys. Subsolidus re-equilibration of the atokite–rustenburgite core with the Cu-rich host is considered unlikely to produce the peripheral zones of the Cu-rich *PGM* around this core. These zoned *PGM* probably formed from a trapped liquid rich in noble metals, Cu, and Sn. Decrease in temperature and increase in activity of Cu in the remaining liquid seem to have been the main factors to control the order of crystallization of the *PGM* in the zoned intergrowths.

Keywords: taimyrite, tatyanaite, platinum-group elements, tin, intermetallic compounds, platinum-group minerals, zoning, sulfide ores, Oktyabr'sky deposit, Noril'sk complex, Siberia, Russia.

SOMMAIRE

Nous décrivons ici l'existence d'une solution solide étendue et méconnue entre taimyrite et tatyanaïte, son analogue à dominance de Pt. Dans cette série, le cuivre occuperait un site distinct. Une substitution impliquant Pd et Cu semble importante, de sorte que la solution solide taimyrite–tatyanaïte montre un écart vers la cabriite, qui leur est semblable du point de vue structural. Ces minéraux du groupe du platine ont été découverts dans le minerai à métaux de base de la mine Oktyabr'sky, dans le complexe de Noril'sk, en Sibérie, Russie. La série taimyrite–tatyanaïte se présente en grains individuels ou en aggrégats, associée à un alliage Ag–Au hétérogène, et aussi à des intercroissances zonées de stannures de Pt–Pd–Cu. Dans la plupart des cas, ces intercroissances se trouvent incluses dans la chalcopyrite et démontrent la séquence de cristallisation suivante, établie selon les critères texturaux et compositionnels: atokite–rustenburgite → tatyanaïte → taimyrite riche en Pt → taimyrite appauvrie en Pt → alliage tardif à Ag–Au. Nous ne retenons pas l'hypothèse d'un ré-équilibrage subsolidus impliquant un coeur de la série atokite–rustenburgite avec l'hôte riche en cuivre pour expliquer une périphérie enrichie en minéraux du groupe du platine. En revanche, nous préconisons une cristallisation de ces minéraux à partir d'un liquide résiduel piégé, enrichi en métaux nobles, cuivre et étain. Une baisse de la température et une augmentation de l'activité du cuivre dans ce liquide semblent rendre compte de l'ordre de cristallisation des minéraux du groupe du platine dans ces intercroissances zonées.

(Traduit par la Rédaction)

Mots-clés: taimyrite, tatyanaïte, éléments du groupe du platine, étain, composés intermetalliques, minéraux du groupe du platine, zonation, minerai de sulfures, gisement Oktyabr'sky, complexe de Noril'sk, Sibérie, Russie.

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INTRODUCTION

The Noril'sk complex in northern Siberia, Russia, hosts a number of world-class ore deposits of Cu, Ni, and platinum-group elements (*PGE*), which are associated with base-metal sulfides. Intermetallic compounds of Pd, Cu and Sn, which are exceptionally rare in other complexes, are among the main platinum-group minerals (*PGM*) at Noril'sk (Genkin *et al.* 1981). Three natural intermetallic compounds of Pd, Cu, and Sn have been reported: "stannopalladinite", taimyrite and cabriite. A similarity in compositions, optical properties and X-ray powder-diffraction patterns is characteristic of these *PGM*. They are all palladium-dominant and commonly contain low to moderate levels of Pt, with the maximum reported until now of ~15 wt.% Pt in taimyrite (Begizov *et al*. 1982).

The name "stannopalladinite" was introduced by Maslenitskii *et al.* (1947). They provided only bulk compositions of separated grains of this phase (or phases) from Noril'sk: 40–45 wt.% Pd, 15–20 wt.% Pt, 5–12 wt.% Cu and 28–33 wt.% Sn; these data are not sufficient to define a mineral species, and may in fact pertain to a mixture of *PGM*. Genkin *et al.* (1981) proposed that "stannopalladinite" (~6 wt.% Cu) is related to synthetic (hexagonal) Pd_3Sn_2. In contrast, Evstigneeva & Nekrasov (1984) have suggested that it has the formula Pd_5CuSn_2 and is orthorhombic, with $a \simeq 7.88$ Å and $b \simeq c \simeq 3.94$ Å.

Taimyrite is orthorhombic and has the average composition $(Pd_{2.12}Pt_{0.26}Cu_{0.64})_{\Sigma 3.02}$ $(Sn_{0.85}Sb_{0.12}Pb_{0.01})_{\Sigma 0.98}$ at Noril'sk (Begizov *et al.* 1982). A revised formula, $Pd_9Cu_3Sn_4$, was suggested for synthetic taimyrite, the unit-cell parameters of which are $a \simeq c \simeq 7.82$ Å and $b \simeq 3.91$ Å (Evstigneeva & Nekrasov 1984). Tatyanaite, also found at Noril'sk, is the platinum analogue of taimyrite (Barkov *et al.* 2000). Cabriite (ideally Pd_2CuSn) is orthorhombic ($a \simeq b \simeq 7.88$ Å and $c \simeq 3.94$ Å; Evstigneeva & Genkin 1983).

The present study has a twofold objective: (i) by means of quantitative wavelength-dispersion electron-microprobe analyses (EMPA), to establish the extent of solid solution and to determine the principal mechanisms of substitution in the taimyrite–tatyanaite series, and (ii) to characterize the nature of compositional zoning in peculiar intergrowths of Pt–Pd–(Cu)–Sn-rich platinum-group minerals from the Oktyabr'sky (or Oktyabr') deposit, which forms part of the Noril'sk complex.

ANALYTICAL METHOD

The EMPA data were collected using a fully automated JEOL JXA–8900 electron microprobe at McGill University. The operating conditions were 20 kV and 20 nA, and the following X-ray lines (and standards) were used: Pt$L\alpha$ ($PtAs_2$), Pd$L\alpha$ (Pd_3HgTe_3), Cu$K\alpha$ (chalcopyrite), Ni$K\alpha$ (pentlandite), Fe$K\alpha$ (pyrite), Sn$L\alpha$ (SnO_2), Sb$L\alpha$ (stibnite) and Pb$L\alpha$ (PbS). Except for the SnO_2 standard, all of these standards were supplied by CANMET. The standard Pd_3HgTe_3 was re-analyzed using a metallic Pd standard, and its Pd concentration was confirmed. A finely focused beam (≤ 2 µm) was applied in all cases, and the raw data were processed on-line. The minimum limits of detection were <0.05 wt.% for Ni and Fe, ≤0.1 wt.% for Sb, and ≤0.2 wt.% for Pb. The analytical data for tatyanaite are in excellent agreement with those obtained with a Cameca Camebax electron microprobe (Barkov *et al.* 2000).

RESULTS AND DISCUSSION

Zoned intergrowths

Ten grains of intermetallic compounds of Pt, Pd, Cu and Sn from samples of massive sulfide ore at Oktyabr'sky were examined; four of these are composite and consist of zoned aggregates of members of the atokite $(Pd,Pt)_3Sn$ – rustenburgite $(Pt,Pd)_3Sn$ and taimyrite – tatyanaite solid-solution series. These grains occur in the massive sulfide ore, mainly composed of chalcopyrite and, probably, a sulfide(s) related to chalcopyrite (*e.g.*, mooihoekite, talnakhite or putoranite). Pentlandite, cubanite (or isocubanite), pyrrhotite, and galena occur in subordinate quantities; magnetite and calcite are common accessories in the ore. In the patches of the zoned intergrowths, the atokite–rustenburgite and tatyanaite richest in Pt typically appear in central areas of the composite grains, which reach ~1 mm in the longest dimension. Toward the edge, atokite–rustenburgite gives way in turn to tatyanaite, unusually Pt-rich taimyrite and taimyrite poorer in Pt. An Ag–Au alloy, highly heterogeneous in composition, rims these composite patches (Fig. 1) and occurs in a close association with aggregates of Pt-rich taimyrite – tatyanaite solid-solution series (Fig. 2). The zoned intergrowths are commonly, but not necessarily, enclosed in chalcopyrite or the chalcopyrite-related sulfide(s). We also observed a composite grain hosted by the Ag–Au alloy; it consists of atokite–rustenburgite in the core and taimyrite–tatyanaite in the rim (Figs. 3, 4).

The cryptically zoned Pt-rich taimyrite – tatyanaite in the composite grains shows a progressive decrease in the content of Pt and a complementary increase in Pd toward the rim of the zoned intergrowth. In contrast, the concentration of Cu (and Sn) varies little (Fig. 5).

Compositional variation in the taimyrite–tatyanaite solid-solution series

The compositional spectrum of the taimyrite–tatyanaite series was established on the basis of 237 electron-microprobe analyses, carried out using the same instrument, set of standards and analytical conditions; the totals recorded are mainly between 99 and 101 wt.%. Representative results are presented in Tables 1

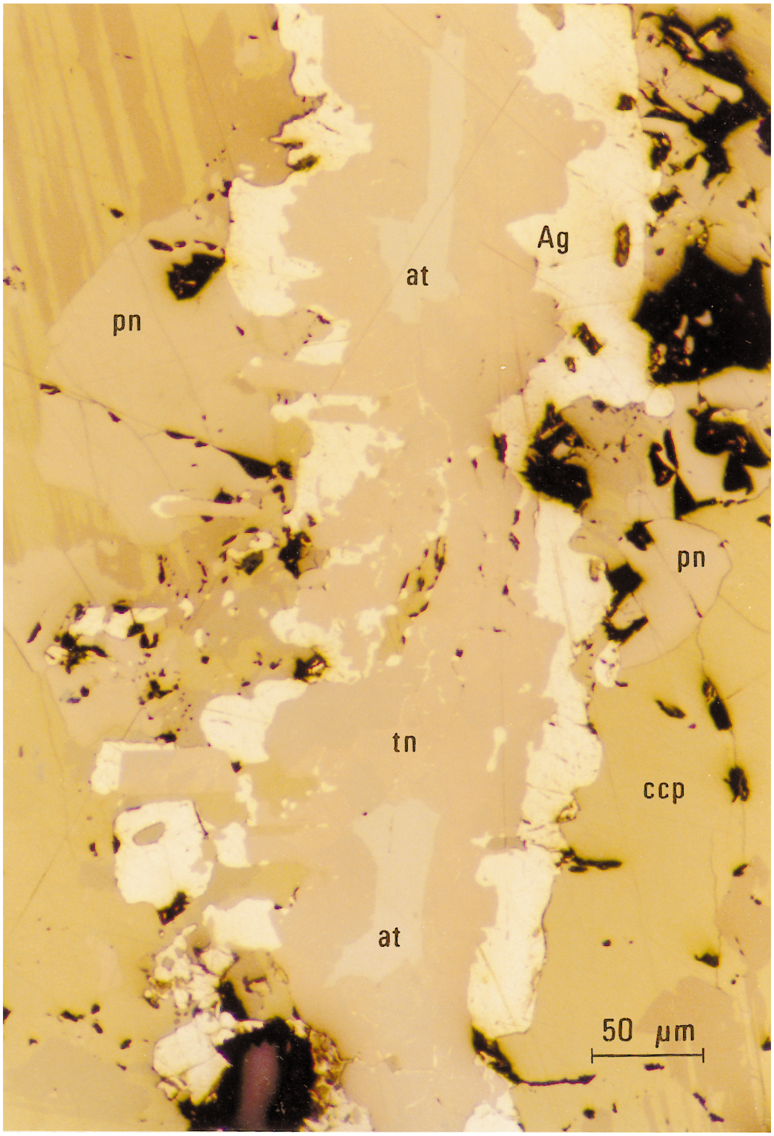

FIG. 1. Zoned intergrowth of atokite–rustenburgite (at), tatyanaite–taimyrite (tn) and heterogeneous Ag–Au alloy (Ag) ($Ag_{0.53-0.89}Au_{0.47-0.11}$; energy-dispersion electron-microprobe data) among chalcopyrite (ccp), cubanite or isocubanite (lamellae within chalcopyrite) and pentlandite (pn). Reflected-light photomicrograph. Scale bar: 50 µm.

to 3. The tatyanaite solid-solution and taimyrite from the type locality at Noril'sk (supplied by V.D. Begizov & V.N. Yakovenchuk) were characterized by X-ray powder diffraction (Barkov *et al.* 2000); the patterns obtained display strong similarities with each other and also with the pattern of synthetic taimyrite of Evstigneeva & Nekrasov (1984). Thus, we infer that members of the taimyrite–tatyanaite series are isostructural.

An inverse linear correlation of Pd and Pt (correlation coefficient R = –0.997; Fig. 6a) indicates that Pt substitutes for Pd in the structure. Although the concentration of Cu varies only slightly in the members richer in Pt, it does so to a greater extent in compositions richer in Pd. The concentration of Cu correlates positively with that of Pt (R = 0.70) and negatively with Pd (R = –0.73). Thus a Pd-for-Cu substitution appears to be important

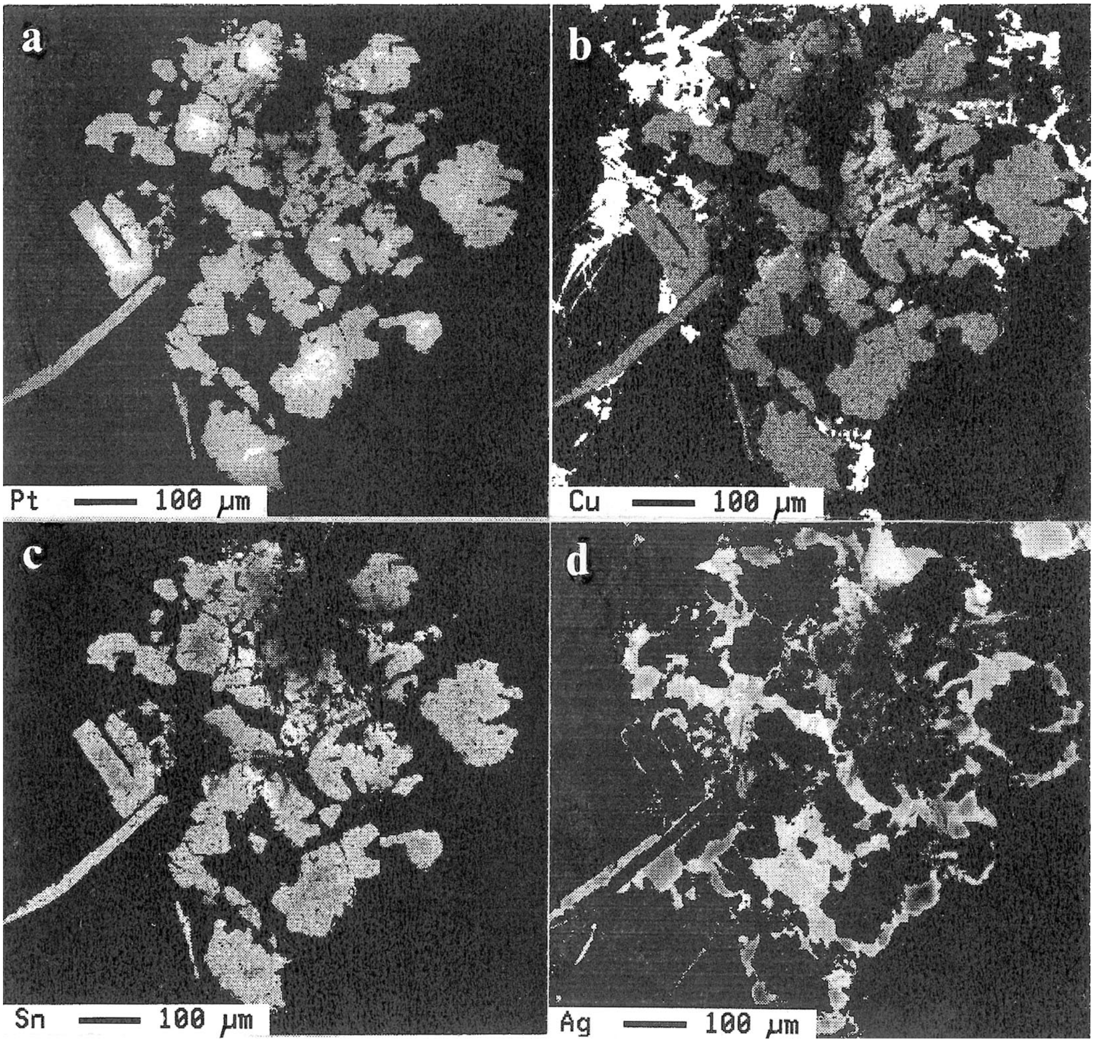

FIG. 2. X-ray maps showing distribution of platinum (a), copper (b), tin (c) and silver (d) in an aggregate of Pt-rich taimyrite – tatyanaite solid solution and in associated Ag–Au alloy. Host: base-metal sulfides (pentlandite and subordinate chalcopyrite). Scale bar: 100 µm.

in these minerals. The plot of Pd + Pt *versus* Cu shows a rather extensive trend for the taimyrite–tatyanaite series, which extends toward cabriite (Fig. 6b).

On the triangular plot Pd–Pt–Cu, members of the taimyrite–tatyanaite solid solution generally plot along the line Cu = 30 atomic % (Fig. 7a). However, the compositions richest in Pd display some deviation from this trend, toward the composition of synthetic (Pt-free) taimyrite (Fig. 7a). This relative decrease in Cu is ascribed to a Pd-for-Cu substitution. The plot (Pd + Pt) – Cu – Sn (Fig. 7b) indicates the existence of an extensive series between taimyrite–tatyanaite and cabriite. Taimyrite, cabriite, "stannopalladinite" (Pd_5CuSn_2) and tatyanaite are structurally closely related and thus may display considerable mutual solid-solution.

Concentrations of Ni and Fe are very low in this series (Table 1). In contrast, sorosite, a Cu-rich stannide, Cu(Sn,Sb) (Barkov *et al.* 1998), contains up to 3.9 wt.% Fe and 1.3 wt.% Ni, which are incorporated *via* the coupled substitution Fe (+ Ni) + Sb → Cu + Sn (Barkov *et al.*, in prep.).

Antimony (<0.01–0.09 atoms per formula unit, *apfu*; Σ atoms = 4) and Pb (0.0–0.03 *apfu*), which substitute for Sn (0.87–1.03 *apfu*), are distributed heterogeneously in the grains of taimyrite–tatyanaite; both display a negative correlation with Sn (*R* = –0.89 and –0.78).

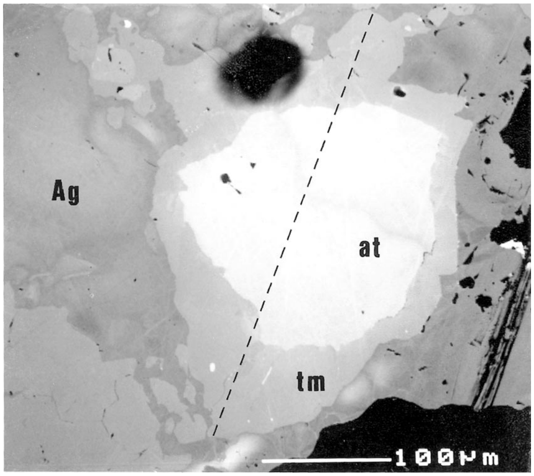

FIG. 3. A grain of atokite–rustenburgite (at), which consists of two domains and is surrounded by cryptically zoned taimyrite–tatyanaite (tm). These platinum-group minerals (*PGM*) are enclosed within a 1-mm grain of heterogeneous Ag–Au alloy (Ag), which is in contact with galena. The Ag–Au alloy in immediate contact with the *PGM* is poor in Cu (≤1.5 wt.% Cu; $Ag_{0.64–0.98}Au_{0.33–0.01}Cu_{0.03–0}$: EDS electron-microprobe data). Back-scattered electron (BSE) image. Scale bar: 100 µm.

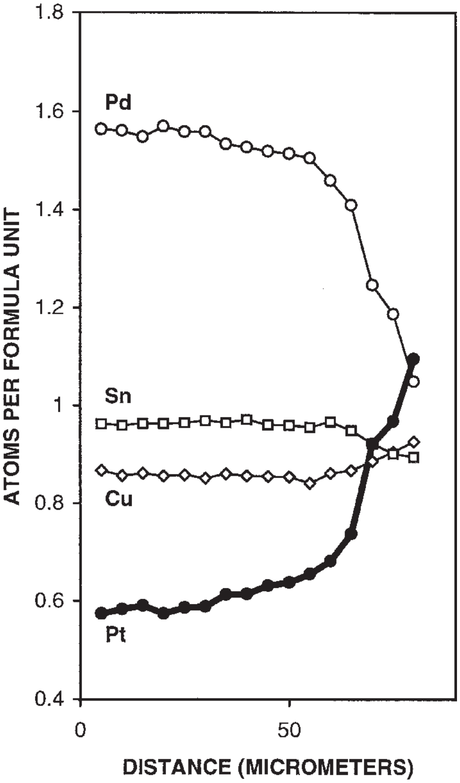

FIG. 5. Example of cryptic zoning in the taimyrite–tatyanaite, sampled along part of the electron-microprobe traverse shown in Figure 4. Note strongly antipathetic variations in Pt and Pd and nearly invariant content of Cu (and Sn). Symbols are the same as in Figure 4 .

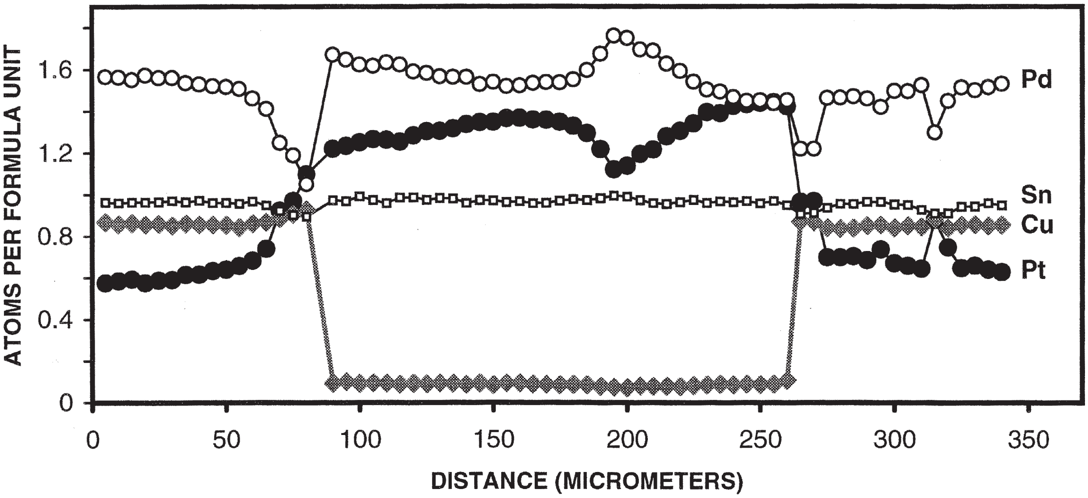

FIG. 4. Compositional variation (atoms per formula unit; Σ atoms = 4) along electron-microprobe traverse across the zoned intergrowth; location of this traverse (dashed line) is shown in Figure 3. Symbols are open circles for Pd, filled circles for Pt, diamonds for Cu, and squares for Sn.

TABLE 1. RESULTS OF SELECTED ELECTRON-MICROPROBE ANALYSES[§] OF THE TAIMYRITE-TATYANAITE SERIES FROM NORIL'SK, SIBERIA

No.	Pt	Pd	Cu	Fe	Ni	Sn	Sb	Pb	Total
1	47.67	17.24	10.76	n.d.	0.15	22.52	0.24	n.d.*	98.58
2	45.77	18.95	10.82	n.d.	0.14	22.86	0.30	n.d.	98.84
3	45.01	19.62	11.35	0.03	0.20	23.24	0.09	n.d.	99.54
4	43.68	21.62	10.54	0.04	0.12	23.83	0.23	n.d.	100.06
5	41.90	21.83	11.07	0.09	0.18	23.54	0.15	n.d.	98.76
6	40.63	22.69	11.11	n.d.	0.12	23.70	0.89	n.d.	99.14
7	40.17	23.67	10.63	0.02	0.12	23.72	0.97	n.d.	99.30
8	39.76	23.93	11.10	n.d.	0.11	24.34	0.49	n.d.	99.73
9	37.89	25.48	11.33	0.13	0.17	24.87	0.19	n.d.	100.06
10	37.21	25.72	11.52	0.16	0.19	25.03	0.21	n.d.	100.04
11	36.11	26.65	11.23	n.d.	0.07	24.90	0.41	n.d.	99.37
12	35.85	26.91	11.69	n.d.	0.07	24.78	0.32	n.d.	99.62
13	35.36	27.23	11.24	n.d.	0.08	25.02	0.42	n.d.	99.35
14	34.01	28.58	11.62	0.02	0.06	25.16	0.39	n.d.	99.84
15	33.82	28.62	11.58	n.d.	0.07	25.11	0.28	n.d.	99.48
16	32.17	29.41	11.74	0.02	0.05	25.65	n.d.	n.d.	99.04
17	31.73	30.67	11.79	0.02	0.03	25.50	0.33	n.d.	100.07
18	31.37	30.95	11.76	0.02	0.05	25.49	0.60	n.d.	100.24
19	30.74	32.44	11.64	0.02	0.08	24.58	0.52	0.19	100.21
20	29.78	33.98	11.59	n.d.	0.07	24.66	0.62	0.27	100.97
21	28.75	33.60	11.83	n.d.	0.06	24.82	0.71	n.d.	99.77
22	27.82	34.60	11.76	n.d.	0.07	24.53	1.15	n.d.	99.93
23	27.04	35.50	11.93	n.d.	0.06	25.04	0.66	0.26	100.49
24	26.38	35.81	11.98	0.02	0.03	25.40	0.65	0.20	100.47
25	25.43	36.72	11.97	n.d.	0.03	25.47	0.77	n.d.	100.39
26	24.93	37.04	12.26	n.d.	0.03	25.44	0.72	n.d.	100.42
27	22.16	39.87	11.69	n.d.	0.07	24.98	1.02	0.50	100.29
28	20.54	40.82	12.13	n.d.	0.07	25.92	0.47	0.50	100.45
29	19.76	41.27	11.95	0.02	0.04	25.91	0.22	0.77	99.94
30	19.12	42.45	11.90	n.d.	0.03	26.20	0.12	1.01	100.83
31	18.46	42.86	11.77	0.02	0.03	25.57	0.30	1.07	100.08
32	17.88	43.52	11.87	n.d.	0.03	25.68	0.51	1.21	100.70
33	17.56	42.84	11.71	0.02	n.d.	25.32	0.72	1.53	99.70
34	16.66	44.44	11.78	0.04	0.04	25.40	1.38	1.02	100.76
35	15.37	45.38	11.96	n.d.	n.d.	24.45	2.52	0.80	100.48
36	15.06	45.75	12.13	n.d.	n.d.	24.53	2.15	0.92	100.54
37	14.77	45.29	11.90	0.02	0.03	24.51	2.49	0.95	99.96
38	14.44	46.02	11.85	n.d.	n.d.	24.77	1.86	1.01	99.95
39	14.12	46.59	12.07	n.d.	n.d.	24.65	2.03	0.88	100.34
40	13.79	46.67	12.24	0.14	n.d.	24.31	2.06	1.06	100.27

[§] JEOL JXA-8900 electron microprobe (McGill University). The analytical results (in weight %) are listed in order of decreasing content of Pt. n.d.: not detected. * <0.2 wt.% Pb.

Formula

The compositions obtained in this study (recalculated on the basis of Σ atoms = 16 and 4; Tables 2 and 3) confirm the 3:1 ratio for (Pd + Pt + Cu) : Sn(+ Sb + Pb), in agreement with the formulae $(Pd,Cu,Pt)_3Sn$ (Begizov & Sluzhenikin 1976, Begizov *et al.* 1982) and $Pd_9Cu_3Sn_4$ (Evstigneeva & Nekrasov 1984). The existence of a distinct *Cu* site in the structure is suggested by our analytical results (Fig. 7a), 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).

The results for the taimyrite–tatyanaite series are consistent with the generalized formulae $(Pd,Pt)_{2+x}Cu_{1-x}(Sn,Sb)$ (where $0 < x < 0.2$) and $(Pd,Pt,Cu)_9Cu_3(Sn,Sb)_4$. As these formulae indicate, the Pd may partly substitute for Cu and enters the *Cu* site, or, alternatively, as much as ~0.7 *apfu* Cu may substitute for Pd, and it enters the *Pd–Pt* site. A structural study is required to determine which version is correct.

Zoning in atokite–rustenburgite

The associated atokite–rustenburgite displays a skeletal habit (Fig. 8), here attributed to difficult nucleation

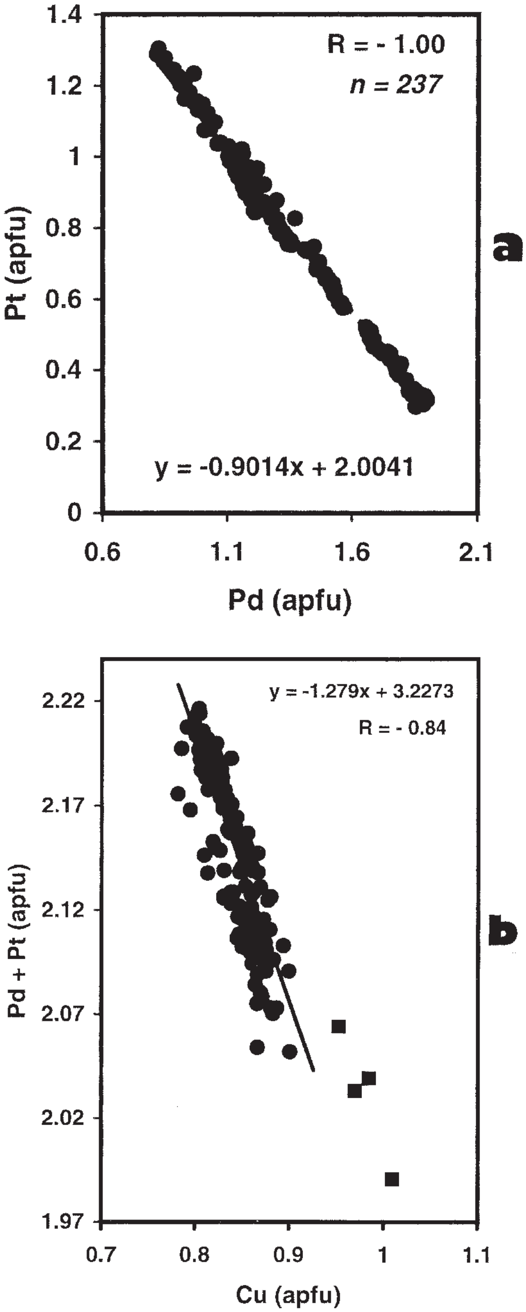

FIG. 6. Concentration of Pt *versus* Pd (a) and of (Pd + Pt) *versus* Cu (b) (in atoms per formula unit; Σ atoms = 4) for the taimyrite–tatyanaite series from Noril'sk. Results of two hundred and thirty-seven analyses (circles; this study) are plotted, along with four representative compositions of cabriite (squares; Evstigneeva & Genkin 1983). The trends and regressions shown on these plots are based on the taimyrite–tatyanaite set of compositions only (this study).

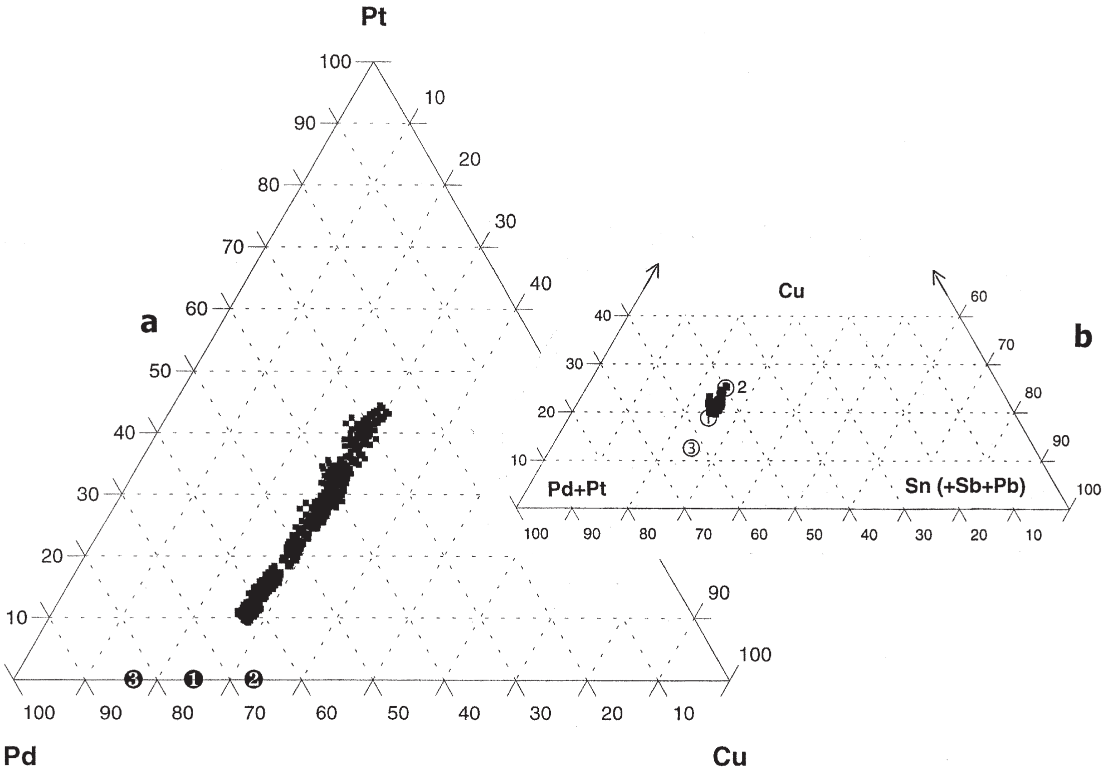

FIG. 7. Compositional variation of members of the taimyrite–tatyanaite series from Noril'sk (filled symbol; this study: *n* = 237) in terms of triangular plots Pd–Pt–Cu (a) and, in the inset (b), (Pd + Pt) – Cu – Sn(+ Sb + Pb); atomic proportions. Four representative compositions of cabriite (Evstigneeva & Genkin 1983) also are plotted in the inset. The numbers 1, 2 and 3 (circles) are ideal compositions of taimyrite, cabriite and "stannopalladinite", respectively (Evstigneeva & Nekrasov 1984).

and competition with the coexisting *BMS* during growth, or to a rapid crystallization. The crystal is compositionally zoned (Fig. 9); a thin "zone" rich in Pd and poor in Pt is observed around an internal cavity that is filled by chalcopyrite. It is likely that this "inclusion" simply reflects an exposure of the subjacent chalcopyrite in the randomly oriented section. An electron-microprobe traverse reveals a steep compositional gradient (Table 4). The content of Pt (*i.e.*, the rustenburgite component) decreases progressively, and that of Pd (*i.e.*, the atokite component) increases toward the edge. Near the cavity, these trends bend sharply, and the level of Pd increases, whereas that of Pt decreases (Fig. 10).

Origin of the zoning

Textural and compositional evidence suggests the following sequence of crystallization, which is quite typical for the zoned intergrowths: atokite–rustenburgite → tatyanaite → Pt-rich taimyrite → taimyrite poorer in Pt → a rim of Ag–Au alloy. The observations of Razin *et al.* (1976) on similar material from Noril'sk are in agreement; they noted that a taimyrite-related phase, which is relatively poor in Pt, replaces the earlier atokite–rustenburgite, and this phase itself is cut and replaced by the late Au–Ag alloy. Genkin & Evstigneeva (1986) suggested that the Cu-rich stannides of Pd and Pt formed later than the associated Cu-poor stannides.

Evstigneeva & Nekrasov (1984) noted that "the formation of rims of Cu-bearing intermetallic compounds around atokite may be explained in terms of their independent crystallization at different times, from solutions in which the activity of Cu increased, and also as a result of solid-state diffusion of Cu in the atokite. A.D. Genkin (oral commun. to T.L. Evstigneeva) favors the latter point of view. However, if the suggestion on the solid-state diffusion is correct, the same orientation of the rim(s) and the central crystal would be expected, but this is not observed. An inhomogeneous distribution of Cu at the margin would be inevitable, and this also does not take a place. Thus, the idea on the crystallization at different times seems more correct".

In the intergrowths examined, the uniform orientation of the Cu-poor core (or relics of a core) and the

TABLE 2. ATOMIC PROPORTIONS[§] (Σ ATOMS = 16) OF THE TAIMYRITE-TATYANAITE SERIES FROM NORIL'SK

No.	Pt	Pd	Cu	Ni	Fe	Σ	Sn	Sb	Pb	Σ
1	5.08	3.37	3.52	0.05	--	12.02	3.94	0.04	--	3.98
2	4.81	3.65	3.49	0.05	--	12.00	3.95	0.05	--	4.00
3	4.65	3.72	3.60	0.07	0.01	12.05	3.95	0.01	--	3.96
4	4.49	4.07	3.33	0.04	0.01	11.94	4.02	0.04	--	4.06
5	4.31	4.11	3.49	0.06	0.03	12.00	3.97	0.02	--	3.99
6	4.14	4.24	3.47	0.04	--	11.89	3.97	0.15	--	4.12
7	4.09	4.42	3.32	0.04	<0.01	11.88	3.97	0.16	--	4.13
8	4.00	4.42	3.43	0.04	--	11.89	4.03	0.08	--	4.11
9	3.75	4.62	3.44	0.06	0.04	11.91	4.05	0.03	--	4.08
10	3.67	4.65	3.49	0.06	0.06	11.93	4.05	0.03	--	4.08
11	3.58	4.85	3.42	0.02	--	11.87	4.06	0.07	--	4.13
12	3.53	4.86	3.53	0.02	--	11.94	4.01	0.05	--	4.06
13	3.50	4.93	3.41	0.03	--	11.87	4.07	0.07	--	4.14
14	3.31	5.10	3.47	0.02	<0.01	11.91	4.03	0.06	--	4.09
15	3.30	5.12	3.47	0.02	--	11.91	4.03	0.04	--	4.07
16	3.13	5.24	3.50	0.02	<0.01	11.90	4.10	--	--	4.10
17	3.05	5.39	3.47	0.01	<0.01	11.93	4.02	0.05	--	4.07
18	3.00	5.43	3.45	0.02	<0.01	11.91	4.01	0.09	--	4.10
19	2.93	5.67	3.41	0.03	<0.01	12.05	3.85	0.08	0.02	3.95
20	2.81	5.87	3.36	0.02	--	12.06	3.82	0.09	0.02	3.93
21	2.73	5.84	3.44	0.02	--	12.03	3.87	0.11	--	3.98
22	2.62	5.98	3.40	0.02	--	12.02	3.80	0.17	--	3.97
23	2.52	6.08	3.42	0.02	--	12.04	3.84	0.10	0.02	3.96
24	2.45	6.11	3.42	0.01	<0.01	12.00	3.88	0.10	0.02	4.00
25	2.36	6.24	3.41	0.01	--	12.02	3.88	0.11	--	3.99
26	2.30	6.26	3.47	0.01	--	12.04	3.85	0.11	--	3.96
27	2.03	6.70	3.29	0.02	--	12.04	3.76	0.15	0.04	3.95
28	1.86	6.78	3.37	0.02	--	12.03	3.86	0.07	0.04	3.97
29	1.80	6.88	3.34	0.01	<0.01	12.04	3.87	0.03	0.07	3.97
30	1.72	7.00	3.29	0.01	--	12.02	3.87	0.02	0.09	3.98
31	1.67	7.11	3.27	0.01	<0.01	12.07	3.80	0.04	0.09	3.93
32	1.60	7.16	3.27	0.01	--	12.04	3.79	0.07	0.10	3.96
33	1.59	7.13	3.26	--	<0.01	11.99	3.78	0.10	0.13	4.01
34	1.49	7.26	3.22	0.01	0.01	11.99	3.72	0.20	0.09	4.01
35	1.36	7.38	3.26	--	--	12.00	3.57	0.36	0.07	4.00
36	1.33	7.42	3.30	--	--	12.05	3.57	0.31	0.08	3.96
37	1.31	7.39	3.25	0.01	<0.01	11.97	3.59	0.36	0.08	4.03
38	1.28	7.51	3.24	--	--	12.03	3.62	0.27	0.09	3.98
39	1.25	7.54	3.27	--	--	12.06	3.58	0.29	0.07	3.94
40	1.21	7.54	3.31	--	0.04	12.10	3.52	0.29	0.09	3.90

[§] The analytical results are listed in Table 1.

TABLE 3. ATOMIC PROPORTIONS[§] (Σ ATOMS = 4) OF THE TAIMYRITE-TATYANAITE SERIES FROM NORIL'SK

No.	Pt	Pd	Cu	Ni	Fe	Σ	Sn	Sb	Pb	Σ
1	1.27	0.84	0.88	0.01	--	3.00	0.99	0.01	--	1.00
2	1.20	0.91	0.87	0.01	--	2.99	0.99	0.01	--	1.00
3	1.16	0.93	0.90	0.02	<0.01	3.01	0.99	<0.01	--	0.99
4	1.12	1.02	0.83	0.01	<0.01	2.98	1.01	0.01	--	1.02
5	1.08	1.03	0.87	0.02	0.01	3.01	0.99	<0.01	--	1.00
6	1.03	1.06	0.87	0.01	--	2.97	0.99	0.04	--	1.03
7	1.02	1.10	0.83	0.01	<0.01	2.96	0.99	0.04	--	1.03
8	1.00	1.10	0.86	0.01	--	2.97	1.01	0.02	--	1.03
9	0.94	1.16	0.86	0.01	0.01	2.98	1.01	0.01	--	1.02
10	0.92	1.16	0.87	0.02	0.01	2.98	1.01	0.01	--	1.02
11	0.90	1.21	0.86	<0.01	--	2.98	1.02	0.02	--	1.04
12	0.88	1.21	0.88	<0.01	--	2.98	1.00	0.01	--	1.01
13	0.87	1.23	0.85	<0.01	--	2.96	1.02	0.02	--	1.04
14	0.83	1.28	0.87	<0.01	<0.01	2.99	1.01	0.02	--	1.03
15	0.83	1.28	0.87	<0.01	--	2.99	1.01	0.01	--	1.02
16	0.78	1.31	0.88	<0.01	<0.01	2.98	1.02	--	--	1.02
17	0.76	1.35	0.87	<0.01	<0.01	2.98	1.01	0.01	--	1.02
18	0.75	1.36	0.86	<0.01	<0.01	2.98	1.00	0.02	--	1.02
19	0.73	1.42	0.85	<0.01	<0.01	3.01	0.96	0.02	<0.01	0.98
20	0.70	1.47	0.84	<0.01	--	3.02	0.96	0.02	<0.01	0.99
21	0.68	1.46	0.86	<0.01	--	3.00	0.97	0.03	--	1.00
22	0.66	1.49	0.85	<0.01	--	3.01	0.95	0.04	--	0.99
23	0.63	1.52	0.85	<0.01	--	3.00	0.96	0.02	<0.01	0.99
24	0.61	1.53	0.86	<0.01	<0.01	3.00	0.97	0.02	<0.01	0.99
25	0.59	1.56	0.85	<0.01	--	3.00	0.97	0.03	--	1.00
26	0.57	1.57	0.87	<0.01	--	3.01	0.96	0.03	--	0.99
27	0.51	1.67	0.82	<0.01	--	3.01	0.94	0.04	0.01	0.99
28	0.47	1.69	0.84	<0.01	--	3.01	0.96	0.02	0.01	0.99
29	0.45	1.72	0.83	<0.01	<0.01	3.00	0.97	<0.01	0.02	1.00
30	0.43	1.75	0.82	<0.01	--	3.00	0.97	<0.01	0.02	0.99
31	0.42	1.78	0.82	<0.01	<0.01	3.02	0.95	0.01	0.02	0.98
32	0.40	1.79	0.82	<0.01	--	3.01	0.95	0.02	0.03	1.00
33	0.40	1.78	0.82	--	<0.01	3.00	0.94	0.03	0.03	1.00
34	0.37	1.82	0.81	<0.01	<0.01	3.01	0.93	0.05	0.02	1.00
35	0.34	1.85	0.81	--	--	3.00	0.89	0.09	0.02	1.00
36	0.33	1.86	0.82	--	--	3.01	0.89	0.08	0.02	0.99
37	0.33	1.85	0.81	<0.01	<0.01	2.99	0.90	0.09	0.02	1.01
38	0.32	1.88	0.81	--	--	3.01	0.91	0.07	0.02	1.00
39	0.31	1.89	0.82	--	--	3.02	0.89	0.07	0.02	0.98
40	0.30	1.88	0.83	--	0.01	3.02	0.88	0.07	0.02	0.97

[§] The analytical results are listed in Table 1.

Cu-rich rim is quite common. For example, the atokite–rustenburgite in the center of the elongate grain, which mainly consists of tatyanaite–taimyrite, has the same orientation as this composite grain (Fig. 1). This example is not inconsistent with a subsolidus reequilibration (or a reaction at a higher temperature) between the early-formed atokite–rustenburgite and the Cu-rich host (*i.e.*, chalcopyrite). The evidence presented in Figure 3, however, indicates that reaction with the Cu-rich host is not necessary to form the zoned intergrowths, as the rim of taimyrite–tatyanaite develops around the atokite–rustenburgite core also in the absence of a Cu-rich phase in contact. In addition, the presence of a nearly continuous rim of an Ag–Au alloy along the *PGM–BMS* border (Fig. 1) would be expected to impede active diffusion of Cu from the *BMS*, another argument in favor of the alternative explanation. For these reasons, we contend that the zoned intergrowths crystallized independently of the host, from a pocket of late-stage *PGE*–Sn–Cu-rich liquid (or fluid); their formation was controlled by a normal decrease in temperature to a large extent. Experimental data support this suggestion. Melting points of pure Pt_3Sn and Pd_3Sn are 1406 (or 1402) and 1326°C, respectively (Shelton *et al.* 1981, and references therein, Durussel *et al.* 1994). Evstigneeva & Nekrasov (1984) reported that in synthetic systems, the ordered Cu–Pd–Sn alloys form at

TABLE 4. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF ZONED ATOKITE-RUSTENBURGITE[§] FROM NORIL'SK

	Weight %					Atomic proportions (Σ atoms = 4)				
	Pt	Pd	Cu	Sn	Total	Pt	Pd	Cu	Σ*M*	Sn
1	39.14	33.68	1.43	21.81	96.68*	1.11	1.75	0.12	2.98	1.02
2	43.57	31.38	0.92	21.53	97.40	1.25	1.65	0.08	2.98	1.02
3	45.69	29.95	0.81	21.24	97.69	1.32	1.59	0.07	2.98	1.01
4	49.33	27.65	0.75	20.81	98.54	1.45	1.48	0.07	3.00	1.00
5	52.22	25.19	0.75	20.52	98.68	1.55	1.37	0.07	2.99	1.00
6	56.64	22.15	0.70	19.97	99.46	1.71	1.23	0.06	3.00	0.99
7	59.42	20.46	0.68	19.74	100.30	1.81	1.14	0.06	3.01	0.99
8	60.10	19.42	0.64	19.40	99.56	1.86	1.10	0.06	3.02	0.98
9	60.17	18.56	0.62	19.34	98.69	1.88	1.06	0.06	3.00	0.99
10	58.07	19.95	0.75	19.76	98.53	1.79	1.13	0.07	2.99	1.00
11	54.37	22.83	0.82	20.18	98.20	1.65	1.27	0.08	3.00	1.01
12	52.74	23.62	0.76	20.25	97.37	1.60	1.32	0.07	2.99	1.01
13	54.45	23.03	0.79	20.02	98.29	1.65	1.28	0.07	3.00	1.00
14	58.06	20.82	0.72	19.97	99.57	1.77	1.16	0.07	3.00	1.00
15	57.32	21.18	0.72	20.02	99.24	1.75	1.18	0.07	3.00	1.00
16	52.78	24.78	0.72	20.43	98.71	1.58	1.36	0.07	3.01	1.00
17	47.52	28.71	0.72	21.16	98.11	1.39	1.54	0.06	2.99	1.01
18	45.97	30.33	0.73	21.42	98.45	1.32	1.60	0.06	2.98	1.01
19	43.98	31.13	0.80	21.57	97.48	1.27	1.64	0.07	2.98	1.02
20	41.06	32.59	0.71	21.64	96.00	1.19	1.72	0.06	2.97	1.03
21	37.90	34.02	0.67	21.69	94.79*	1.10	1.81	0.06	2.97	1.03

[§] Electron-microprobe traverse across the crystal shown in Figure 8 (JEOL JXA-8900 electron microprobe). See Figure 10 for the location of this traverse. Pb (≤0.2 wt.%) and Sb (<0.1 wt.%) were sought, but not detected.

* Semi-quantitative results obtained at the crystal's edge (Fig. 10). The totals include 0.62 wt.% Fe (anal. no. 1) and 0.51 wt.% Fe (anal. no. 21); these concentrations are a result of contamination from neighboring grains.

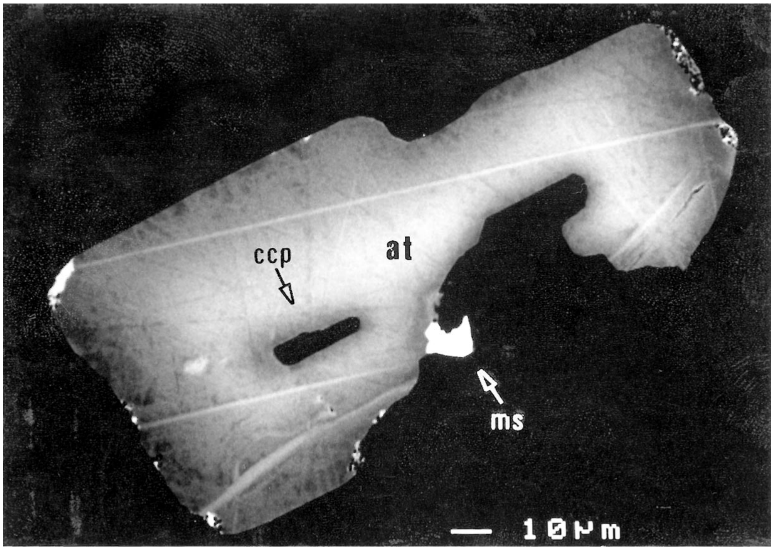

FIG. 8. Skeletal (zoned) crystal of atokite–rustenburgite (at) associated with base-metal sulfides: chalcopyrite (ccp), pyrrhotite and pentlandite. A tiny grain (ms; white) at its contact is maslovite PtTe(Bi,Sb). Back-scattered electron image. Scale bar: 10 μm.

much lower temperatures: 550°C for Pd_5CuSn_2 ("stannopalladinite" analogue), 320°C for $Pd_9Cu_3Sn_4$ (taimyrite analogue), and 198°C for Pd_2CuSn (cabriite analogue). These experiments suggest that Cu-poor rustenburgite and a cabriite-type compound (the richest in Cu among related intermetallic compounds) should be the first and the last, respectively, to form from a liquid rich in Pd, Pt, Cu and Sn during cooling.

The observed textures are consistent with the experimental data. The Cu-poor atokite–rustenburgite in the center of the zoned intergrowths crystallized before taimyrite–tatyanaite. After its crystallization, the activity of Cu in the remaining liquid must have increased. With a significant drop in temperature, tatyanaite–taimyrite deposited around the atokite–rustenburgite core, at the periphery of the zoned intergrowths. The character of the cryptic zoning (*e.g.*, Fig. 5) suggests that incorporation of Pd instead of Pt accompanies a decrease in temperature of crystallization of the taimyrite–tatyanaite solid solution. Apparently, both Ag and Au were totally incompatible during the fractional crystallization of the *PGM*, and their concentrations increased to reach a maximum at the final stage of evolution of the zoned intergrowth, at which point the heterogeneous Ag–Au alloy precipitated (Fig. 1).

The zoned crystal of atokite–rustenburgite (Figs. 8–10) apparently crystallized from the Pt-rich center to the Pd-rich edge; this order of crystallization is consistent with the higher melting point of Pt_3Sn relative to Pd_3Sn. The appearance of the Pd-rich "zone" around the filled cavity may be related to a specific cross-section of the crystal, such that the underlying chalcopyrite and the Pd-rich zone are intersected at the center.

CONCLUSIONS

Our study indicates the existence of newly documented extensive solid-solution series between taimyrite and tatyanaite, in which Pt replaces Pd in the structure. The orthorhombic solid-solution covers a considerable field in the system Pd_3Sn – Pt_3Sn – Cu_3Sn (Fig. 7a). The incorporation of Pd instead of Pt likely accompanies a decrease in temperature of crystallization of the taimyrite–tatyanaite solid solution.

Cu probably occupies a distinct site in the taimyrite-type structure. In addition, there is evidence of a limited Pd-for-Cu substitution in the taimyrite series.

Taimyrite–tatyanaite forms a solid-solution series toward cabriite, which is closely related with taimyrite both compositionally and structurally.

The zoned intergrowths of the Pt – Pd – Cu stannides appear to have formed independently of the host minerals from a pre-existing late-stage liquid rich in Pd, Pt, Cu and Sn. The sequence in which they crystallized (atokite–rustenburgite → tatyanaite → Pt-rich taimyrite → taimyrite poorer in Pt) was mainly controlled by a decrease in temperature and increase in activity of Cu in the remaining liquid.

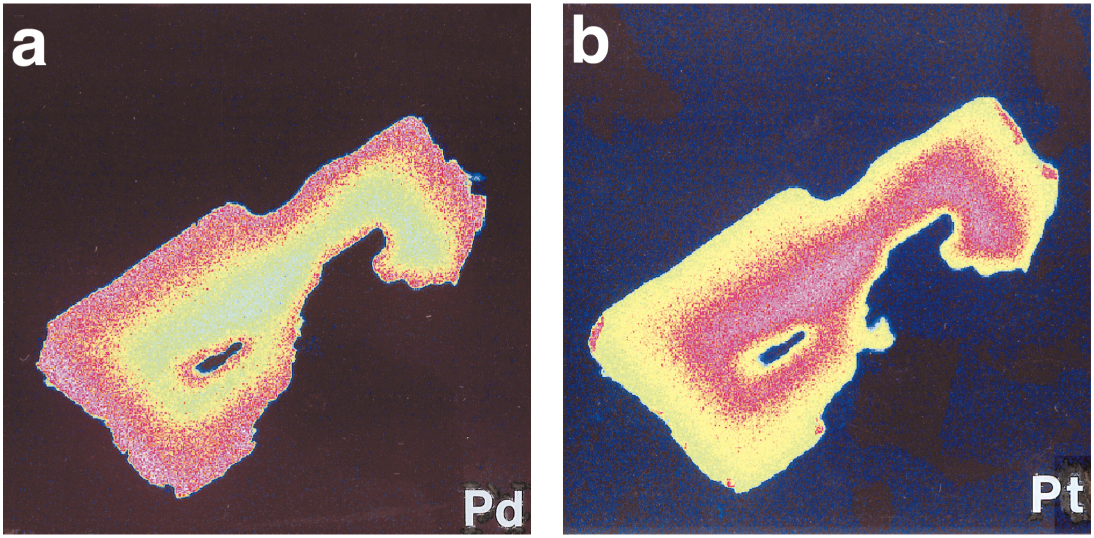

FIG. 9. Palladium and platinum X-ray maps of the zoned crystal of atokite–rustenburgite shown in Figure 8. A general decrease in content of these elements is shown by the change in color: red (highest) → yellow (lower) → green (lowest). The crystal is 0.16 mm in the longest dimension.

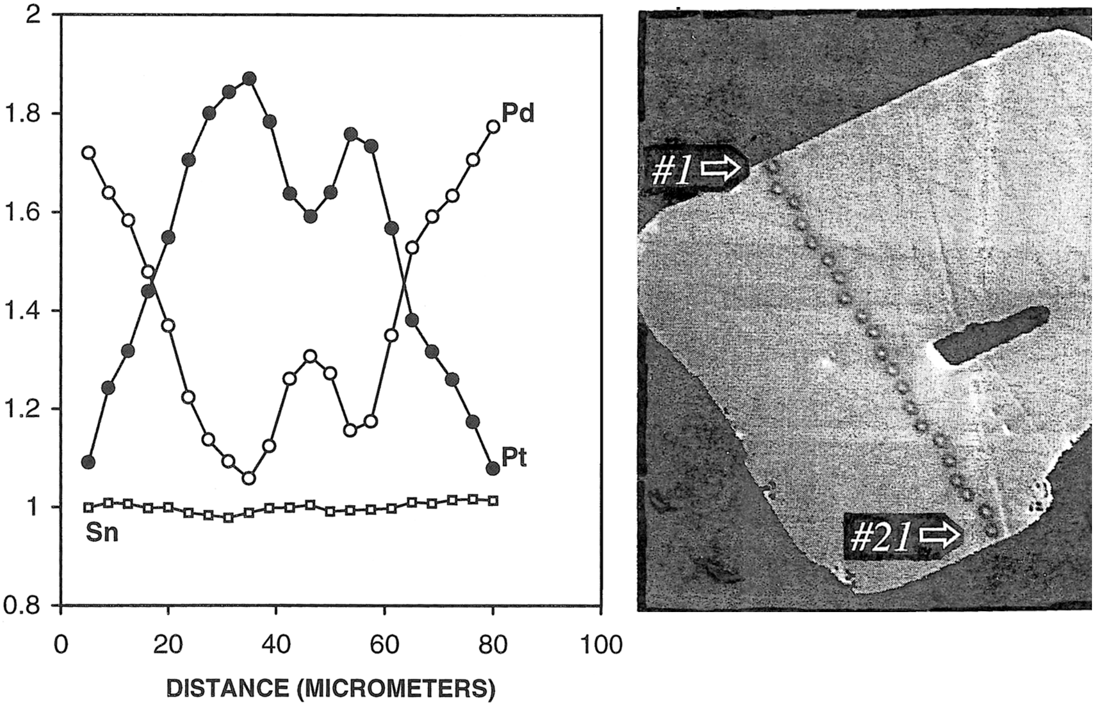

FIG. 10. Compositional variation (atoms per formula unit; Σ atoms = 4) along electron-microprobe traverse across the zoned atokite–rustenburgite (Fig. 8). The location of this traverse is shown in a secondary-electron image in the inset. Note abrupt changes in concentrations of Pt and Pd near the internal cavity (black in the image).

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