# NIGEL J. COOK§ AND CRISTIANA L. CIOBANU

Geological Survey of Norway, N-7491 Trondheim, Norway

## ROLAND K.W. MERKLE

Department of Earth Sciences, University of Pretoria, Pretoria 0002, South Africa

### HEINZ-JÜRGEN BERNHARDT

Institut für Mineralogie, Ruhr-Universität Bochum, D-44780 Bochum, Germany

# Abstract

Compositional data are given for a suite of minerals present in a particularly PGM-rich ore from Noril'sk region, Russia. A characteristic association of altaite (PbTe) intergrown with sobolevskite [Pd(Bi,Te)] and taimyrite [(Pd,Pt,Cu)<sub>3</sub>Sn] occurs within talnakhite–galena-rich ores from the Oktyabr' mine, Noril'sk Complex. Associated minerals include Ag–Au alloy and minor amounts of froodite, paolovite, sperrylite and Pd(Bi,Pb). Varying Bi:Te values in sobolevskite are in agreement with the previously proven solid-solution between kotulskite (PdTe) and sobolevskite (PdBi). New compositional and reflectance data are provided for taimyrite with the composition (Pd<sub>1.55</sub>Cu<sub>0.85</sub>Pt<sub>0.6</sub>)<sub> $\Sigma$ 3</sub>Sn. An alloy with the composition Pt<sub>2</sub>FeCu is common as prismatic and needle-shaped crystals at the outer margin of altaite. This may represent the first report of tulameenite from Noril'sk, albeit morphologically and paragenetically somewhat different from previously reported occurrences. Observed textures, dominated by a range of intergrowths, in part symplectitic, at every scale from cm-size oblong-shaped grains of galena in talnakhite down to  $\mu$ m-scale intergrowths of altaite and sobolevskite, derive from a complex sequence of unmixing in the system Pt–Pd–Bi–Te–Pb–Ag–Au–Sn–Cu–Fe–Ni–S–Te during cooling.

Keywords: platinum-group minerals, sobolevskite, taimyrite, tulameenite, Noril'sk, Russia.

### Sommaire

Ce travail fait état de compositions de minéraux présents dans un minerai particulièrement enrichi en minéraux du groupe du platine de la région de Noril'sk, en Russie. Une association impliquant l'altaïte (PbTe) en intercroissance avec la sobolevskite [Pd(Bi,Te)] et la taimyrite  $[(Pd,Pt,Cu)_3Sn]$  est caractéristique de minerais riches en talnakhite–galène à la mine Oktyabr', complexe de Noril'sk. Leurs sont associés un alliage Ag–Au et des quantités moindres de froodite, paolovite, sperrylite et Pd(Bi,Pb). Le rapport Bi:Te variable de la sobolevskite concorde avec les résultats antérieurs à propos d'une solution solide entre kotulskite (PdTe) et sobolevskite (PdBi). Nous présentons des données nouvelles sur la composition et la réflectance de la taimyrite ayant une composition (Pd<sub>1.55</sub>Cu<sub>0.85</sub>Pt<sub>0.6</sub>)<sub>23</sub>Sn. Un alliage de composition Pt<sub>2</sub>FeCu est répandu en cristaux prismatiques et aciculaires à la bordure de l'altaïte. Il pourrait s'agir du premier exemple de tulameenite à être signalé à Noril'sk, quoique morphologiquement et paragénétiquement différent des exemples contus ailleurs. Les textures observées, en particulier les intercroissances, en partie symplectitiques, à toutes les échelles à partir des grains centimétriques allongés de galène dans la talnakhite jusqu'aux intercroissances millimétriques d'altaïte et de sobolevskite, résultent d'une séquence complexe de démixion dans le système Pt–Pd–Bi–Te–Pb–Ag–Au–Sn–Cu–Fe–Ni–S–Te au cours du refroidissement.

(Traduit par la Rédaction)

Mots-clés: minéraux du groupe du platine, sobolevskite, taimyrite, tulameenite, Noril'sk, Russie.

<sup>§</sup> E-mail address: nigel.cook@ngu.no

# INTRODUCTION

Kotulskite (PdTe, Genkin *et al.* 1963) is a relatively common mineral in a number of PGE mineral deposits (Cabri 1981a). Sobolevskite, its Bi-dominant analogue, (PdBi; Evstigneeva *et al.* 1976) is relatively less common. In this paper, we examine the occurrence of sobolevskite and associated minerals in a sample from the Noril'sk Orefield unusually enriched in the platinumgroup elements (PGE). The paragenesis of platinumgroup minerals (PGM) is described, and reflectance data are given for an intermediate member of the taimyrite– tatyanaite solid-solution series, which characteristically occurs at the margins of altaite–sobolevskite intergrowths. A Pt–Cu–Fe alloy, abundant within altaite, has the composition of tulameenite.

The mineralogy of the Noril'sk and Talnakh ore deposits, situated on the northwestern edge of the Siberian platform in Arctic Russia (Long. 62°21' N, Lat. 88°02' E), was discussed by a number of authors (*e.g.*, Genkin 1968, Genkin *et al.* 1981, Genkin & Evstigneeva 1986, Distler *et al.* 1993, Distler & Kunilov 1994, Tvrdý & Kolesar 1995). Some 280 mineral species are known from Noril'sk, including about 50 or so various platinum-group minerals and incompletely characterized phases. No other deposit is the type locality for such a wide number of PGM, many of which have not been reported from other deposits.

#### DESCRIPTION OF THE SAMPLE

The material investigated is an extremely PGM-rich and particularly spectacular sample of massive ore from the Talnakh deposit, consisting of massive talnakhite with macro-scale subgraphic intergrowths of both galena and pentlandite (Figs. 1a, b). It was collected from the -720 level of the Oktyabr' mine, close to the upper contact of Cu-Ni-PGE-rich ore lens with the gabbroic intrusion, and was kindly donated to the authors by Mr. Vladimir S. Balbin (Noril'sk Nickel Company). Galenarich ores from Noril'sk are almost always strongly enriched in PGE and commonly contain several hundred ppm PGE (total) or even more. Several rare PGM have been found for the first time in such ores (Genkin et al. 1981). The sample matrix, <90% of the sample, is composed of massive talnakhite, Cu<sub>9</sub>(Fe,Ni)<sub>8</sub>S<sub>16</sub>, with subordinate galena, pentlandite and mooihoekite, Cu<sub>9</sub>Fe<sub>9</sub> S<sub>16</sub>, in a series of unmixing and symplectitic intergrowths textures (Figs. 1a-d). Oval blebs of galena up to 1 cm in size and subhedral grains of pentlandite 1-2 mm in size are set within talnakhite. Both appear to represent unmixing from talnakhite or a higher-temperature Cu-Fe sulfide, but blebs of galena characteristically overprint the bodies of pentlandite (Fig. 1d). Small, elongate grains of djerfisherite, the K- and Cl-bearing sulfide, K<sub>6</sub>(Fe,Cu,Ni)<sub>25</sub>S<sub>26</sub>Cl, are associated with galena or PGM or both. Sphalerite and chalcopyrite are accessory phases.

The PGM are associated with rounded, elongate or lobate intergrowths, 1-16 mm in length, consisting dominantly of a symplectite of altaite, PbTe, and sobolevskite, Pd(Bi,Te) (Fig. 1e). Abundant domains of Ag-Au alloy, as rims and veinlets <50 µm in size, surround the PGM and are found within talnakhite close to the PGM intergrowths as a characteristic part of the assemblage (Fig. 1f). The symplectitic intergrowths of altaite, showing a recognizable bright cream-grey color and faint greenish tint against talnakhite, and pale orange-pinkish sobolevskite (Fig. 2a), indicate cocrystallization of the two minerals. Margins against talnakhite are, however, generally free of sobolevskite. Rounded and elongate grains, typically 80-300 µm in diameter, of a reddish brown phase, with distinct reflectance pleochroism (reddish to chocolate brown), strong anisotropy (tan to dark brown with violet tints) and a hardness exceeding that of altaite or sobolevskite occur at the margin of the symplectite against talnakhite (Fig. 2b). These have a composition approximating to (Pd,Pt,Cu)<sub>3</sub>Sn (*i.e.*, taimyrite; see Discussion). Native silver is common at margins between sobolevskite and altaite (Fig. 2c) and throughout the talnakhite matrix. Sobolevskite with inclusions of altaite and Ag-Au alloy also are found as rounded blebs, protruding or enclosed within galena, with flaky grains of talnakhite marking the margin of the blebs (Fig. 3a). Microscopic (<5 µm), pink, needle-shaped grains of a Pt-Cu-Fe alloy (see below) are located within altaite on the outermost margin of the intergrowths (Figs. 2d, 3b-f). Other minerals present in the assemblage in minor amounts are froodite (PdBi<sub>2</sub>) and sperrylite (PtAs<sub>2</sub>), the latter showing a deep grey color against altaite. Smaller domains of PGM occur throughout the talnakhite matrix and as rounded inclusions in galena. In such intergrowths, sobolevskite is dominant. More rarely, a Pb-bearing phase, either plumbian sobolevskite or polarite, also is present. Grains of a grey-brown mineral less than 20 µm across, tentatively identified as telargpalite, (Pd,Ag)<sub>3</sub>Te (Kovalenker et al. 1975), occur intimately intergrown with sobolevskite and native silver. Paolovite, Pd<sub>2</sub>Sn (Genkin et al. 1975) is a trace constituent of some PGM intergrowths (Figs. 3e, f). Both are intergrown with sobolevskite in assemblages in which taimyrite is absent.

## ELECTRON-PROBE MICRO-ANALYSES

Electron-probe micro-analyses were carried out with a CAMECA SX–50 instrument at the Mineralogical Institute, Würzburg, Germany. The following standards and radiations were used: pure Bi ( $M\alpha$ ), pure Pt ( $M\alpha$ ), pure Pd ( $L\alpha$ ), PbS (Pb $M\alpha$ ), FeS<sub>2</sub> (Fe $K\alpha$ , SK $\alpha$ ), pure Cu ( $K\alpha$ ), ZnS (Zn $K\alpha$ ), pure Ni ( $K\alpha$ ), pure Co ( $K\alpha$ ), pure Te ( $L\alpha$ ), pure Se ( $L\alpha$ ), pure Ag ( $L\alpha$ ), pure Cu ( $M\alpha$ ), Sb<sub>2</sub>S<sub>3</sub> (Sb $L\alpha$ ), and SnO<sub>2</sub> (Sn $L\alpha$ ). No other elements were detected in any of the minerals analyzed. Beam current and accelerating voltage were set at 15 nA and 15 kV, respectively. Beam size was 1–2  $\mu$ m, with minimum limits of detection of about 0.05 wt.% for all elements. Mineral grains and standards were analyzed under the same operating conditions.

Mean compositions of talnakhite and pentlandite are  $Cu_{9.03}(Fe_{7.58}Ni_{0.30})_{\Sigma7.88}S_{15.98}$  and  $Fe_{4.70}Ni_{3.86}Co_{0.11}$   $Cu_{0.10})_{\Sigma8.77}S_{8.00}$ , respectively. Galena compositions are close to being stoichiometric, PbS, but minor Bi, Sb, Se and Te were nevertheless present in all cases. Compositional variation in altaite is equally restricted; compositions are close to being stoichiometric, except for small amounts of Cu, Fe, Ag, Zn, Sb, Sn, Bi and Se, close to minimum limits of detection, in some grains (Table 1). Native silver (mean Ag\_{95.3}Au\_{4.7}) and Ag–Au alloy (mean Ag\_{61.8}Au\_{38.2}) were found not to contain admixtures of Cu, Pt, Pd, Bi or Te.

Analytical results on 44 grains of sobolevskite are summarized in Table 2 and show a range in compositions along the PdBi–PdTe join (Fig. 4). Compositions of the reddish brown phase are close to (Pd,Pt)<sub>2.1</sub>Cu<sub>0.9</sub>Sn (Table 3). Compositions of the Pd(Bi,Pb) phase and of the Pt–Cu–Fe alloy are given in Table 4. Because of the very fine grain-size and intergrown character of the latter, the majority of the 26 analyses included some Pb, Te and Bi from adjacent minerals. Exceptions are the two analyses in Table 4, which are both close to Pt<sub>2</sub>FeCu. The compositions of other minerals are not tabulated, as these were found to be close to stoichiometry.

### REFLECTANCE DATA

Reflectance spectra (Fig. 5) were collected for a grain of taimyrite with the composition  $(Pt_{1.55}Pd_{0.60}$   $Cu_{0.85})_{\Sigma_3}Sn$ , using instrumentation similar to that described by Bernhardt (1987): a Leitz Orthoplan microscope and Hamamatsu R1477 photomultiplier system. A Zeiss WTiC standard was used in air and immersion oil (DIN 58.884). Our data compare reasonably well with earlier data for taimyrite (Begizov *et al.* 1982). However, we note a tight fit both to tatyanaite (Barkov *et al.* 2000b) and also to cabriite (Evstigneeva & Genkin 1983), showing that reflectance data can hardly be considered diagnostic among stannides of the stannopaladinite group.

### DISCUSSION

# Pd(Bi,Te)

Since there exist hexagonal, orthorhombic and monoclinic polymorphs of PbBi (Bhatt & Schubert 1979, Genkin *et al.* 1981, Bayliss 1990), it is impossible to say, with total certainty, that the studied grains are indeed members of the sobolevskite–kotulskite series. However, on the basis of optical properties, a tentative identification can nevertheless be made. Indeed, Bayliss (1990) proposed that an admixture of a monoclinic polymorph might explain unindexed reflections in the original description of sobolevskite (Evstigneeva et al. 1975).

Compositions display a limited range of Bi/(Te + Bi + Pb + Sb + Sn) values, from 0.671 to 0.779 (Fig. 4), within the solid solution between kotulskite (PdTe) and sobolevskite (PdBi). Such a relationship was documented in the original description of sobolevskite (Evstigneeva et al. 1976), in which a range of compositions from stoichiometric PdBi to close to end-member kotulskite. PdTe, was reported. Later references to kotulskite and sobolevskite corroborated the existence of a complete solid-solution, with a broad compositional field between the two phases identified in several dozen publications (e.g., Cabri & Laflamme 1981, Vuorelainen et al. 1982, Tarkian 1987, Beaudoin et al. 1990, Mulja & Mitchell 1990, Trofimov et al. 1990, Grokhovskaya et al. 1992, Yakovlev et al. 1991, Barkov & Lednev 1993, Coghill & Wilson 1993, Farrow & Watkinson 1997, Shvedov et al. 1997, Halkoaho et al. 1998, Mitrofanov et al. 1998). Li & Naldrett (1993a) reported the occurrence of Te-free sobolevskite, *i.e.*, the end member, from the Strathcona deposit, Sudbury, Ontario. Compositions approaching Bi/(Te + Bi) = 0.5, *i.e.*, near the boundary between kotulskite and sobolevskite, have been reported from Blue Lake, Labrador Trough, Quebec (Beaudoin et al. 1990) and the Burakovsky Complex, Karelia (Trofimov et al. 1990). Kotulskite and sobolevskite are both hexagonal, with comparable unitcell parameters (a 4.19, 4.23; c 5.67, 5.69 Å, respectively). Evstigneeva et al. (1975) reported similar X-ray data, hardness and reflectance spectra for the two endmembers.

Although not named as such, and as pointed out by Beaudoin *et al.* (1990), unnamed minerals UN 1976–5, UN 1973–18, and possibly also UN 1979–1 (Cabri 1981b) plot close to the solid-solution join in Pd–Te–Bi space, with UN 1973–18 (Razin *et al.* 1975) being close

TABLE 1. COMPOSITIONS OF GALENA AND ALTAITE, NORIL'SK OREFIELD, RUSSIA

	Galena			Altaite		
	$\frac{1}{n=5}$	Max.	Min.	Mean $n = 17$	Max.	Min.
Cu wt.%	-	-	-	0.28	0.61	
Fe	-	-	-	0.07	0.38	-
Ag	-	-	-	-	0.12	-
Zn	-	-	-	-	0.13	-
Pb	85.91	86.33	85.33	61.33	62.02	60.40
Sb	0.09	0.17	-	0.32	0.60	-
Sn	-	-	-	0.07	0.38	-
Bi	0.33	0.48	0.19	0.10	0.31	-
S	12.98	13.03	12.92	-	-	-
Te	0.73	0.95	0.55	37.33	37.98	35.84
Se	0.13	0.15	0.11	0.06	0.29	-
Total	100.17			99.56		

Note: - indicates below minimum detection limit (0.05 wt.%).

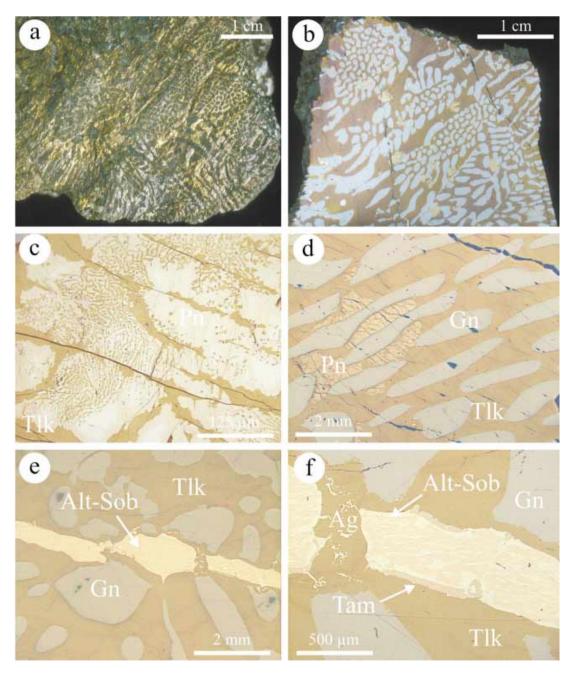


FIG. 1. (a) Massive talnakhite – galena – pentlandite – PGM ore. Subgraphic intergrowth of galena (dark) and talnakhite on unpolished surface. (b) Polished surface of sample showing intergrowth of galena (grey) within tarnished talnakhite (pinkish brown). Minor amounts of pentlandite (yellow) are visible. (c–e) Photomicrographs in reflected light. (c) Symplectitic intergrowth of pentlandite (Pn) in talnakhite (Tlk). (d) Lens-shaped blebs of galena (Gn) in talnakhite (Tlk), overprinting earlier exsolution-induced bodies of pentlandite (Pn). (e) Occurrence of PGM as elongate segregations (Alt–Sob) within talnakhite (Tlk) – galena (Gn) matrix. (f) Detail of area in Figure 2e, showing intergrowths of altaite and sobolevskite, with elongate grains of taimyrite (Tam) along grain margins. Silver (Ag) occurs as irregularly shaped masses at grain margins and in the talnakhite (Tlk) – galena (Gn) matrix.

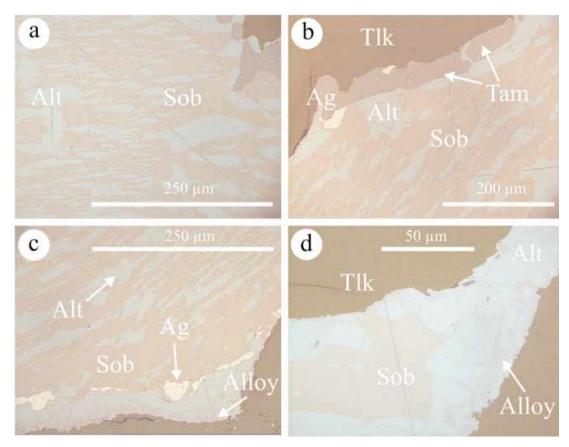


FIG. 2. Photomicrographs in reflected light. (a) Intergrowths of altaite (Alt) and sobolevskite (Sob). (b) Close-up of margin of altaite (Alt) – sobolevskite (Sob) intergrowth, showing elongate grains of taimyrite (Tam) and native silver (Ag). (c) Margin of altaite (Alt) – sobolevskite (Sob) intergrowth showing native silver (Ag) between sobolevskite and altaite and tiny grains of Pt<sub>2</sub>FeCu alloy at outer margin. (d) Close-up of the margin of altaite–sobolevskite intergrowths showing needle-shaped pink crystals of Pt<sub>2</sub>FeCu.

to end-member sobolevskite. Furthermore, unknown mineral UK2 (Coghill & Wilson 1993), and "polarite" from Messina, Transvaal (Tarkian 1987), are probably also Te-bearing sobolevskite, as is UN 1976–5 (Stumpfl & Tarkian 1976), which also contains significant Sb.

There would appear to be complete solid-solution between kotulskite and sudburyite (PdSb; Cabri & Laflamme 1974), which shares hexagonal symmetry and belongs to the same space group as kotulskite and sobolevskite. Natural members of the series containing Sb (either stiboan sobolevskite or stiboan kotulskite or bismuthoan sudburyite) have been reported in several studies (*e.g.*, Evstigneeva *et al.* 1976, Edgar *et al.* 1989, Tolstykh *et al.* 1997). Dobrovol'skaya *et al.* (1985) reported compositions intermediate in the PdBi–PdSb series, containing 19.01 and 27.13 wt.% Sb (two point analyses). In turn, sudburyite may contain up to 15 wt.% combined (Te + Bi) (Cabri & Laflamme 1981). In the present study, Sb contents do not exceed 1.7 mol.% PdSb.

Most grains of sobolevskite analyzed in this study contain significant Pb (up to 3.44 wt.% in sobolevskite associated with altaite, although back-scattered electron images did not reveal intergrowths at the submicrometer scale). A distinctly Pb-rich variety, either plumboan sobolevskite or polarite, is also noted (Table 4). Questions of nomenclature among these minerals have been addressed by Evstigneeva & Genkin (1990), who distinguished two end-members, informally labeled "plumbopolarite" (PdPb) and "bismuthopolarite" (PdBi).

Kovalenker *et al.* (1973) documented comparable levels of substitution of Pb for (Bi,Te) in kotulskite from Noril'sk. Varieties appreciably richer in Pb, containing up to 9.5 wt.% Pb, were reported by Watkinson & Ohnenstetter (1992). In the absence of structural data, it is impossible to identify these phases with full certainty,

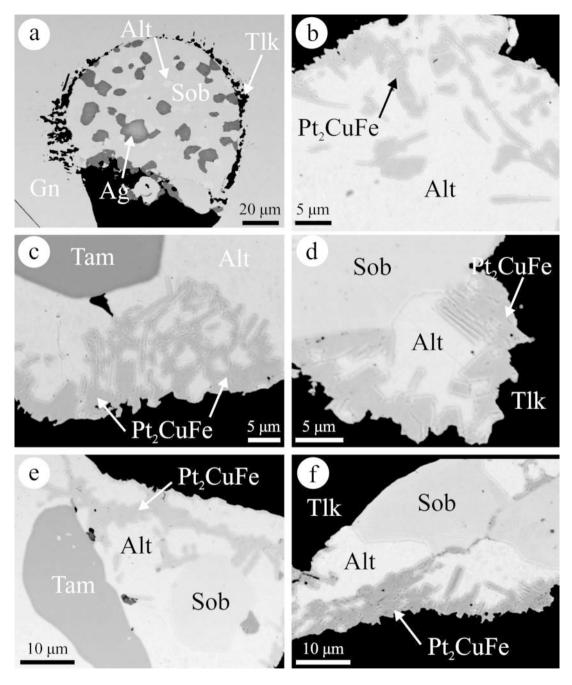


FIG. 3. Back-scattered electron images. (a) Rounded bleb of sobolevskite (Sob) within galena (Gn), containing inclusions of altaite (Alt) and native silver (Ag). Margins between sobolevskite and galena are marked by talnakhite (Tlk). (b)–(f) Skeletal, prismatic and needle-shaped aggregates of Pt<sub>2</sub>CuFe alloy (tulameenite?) enclosed within altaite, close to the outer margin of the intergrowths with talnakhite. Sob: sobolevskite, Alt: altaite, Tam: taimyrite.

owing to the existence of polymorphs and as yet incompletely defined solid-solution series in the Pd–Bi–Te– Pb system. Polarite [Pd(Bi,Pb)] (Genkin *et al.* 1969) is orthorhombic and isostructural with synthetic PdBi (Yushko-Zakharova *et al.* 1974). Pt-bearing varieties of sobolevskite also have been reported [*e.g.*, (Pd<sub>0.67</sub>Pt<sub>0.29</sub>  $Fe_{0.11}$ ) $\Sigma_{1.07}$ (Bi<sub>0.70</sub>Sb<sub>0.23</sub>) $\Sigma_{0.93}$ : Rudashevsky *et al.* 1992], yet the extent of solid solution toward Pt end-members is unknown. In addition, evidence of a solid solution between Pd(Te,Bi) toward NiTe, in an undetermined crystal system, also has been presented (*e.g.*, Cabri & Laflamme 1976, Marchetto 1990).

TABLE 2. COMPOSITIONS OF SOBOLEVSKITE, NORIL'SK OREFIELD, RUSSIA

	1	Max.	Min.	2	3	4	5	6	7	8
	Mean									
Pd wt.%	35.47	36.55	34.29	35.55	34.85	34.56	35,16	35.04	36.55	36.10
Pt	0.11	0.57	-	0.18	0.34	0.21	-	-	-	-
Ni	-	0.11	-	-	0.10	-	-	-	-	-
Cu	0.12	0.49	-	-	-	-	-	0.17	0.14	0.19
Zn	-	0.21	-	-	-	-	0.21	0.10	-	-
Рb	2.10	3.44	1.09	3.44	1.10	1.31	3.18	2.22	2.10	1.34
Sb	0.09	0.44	-	-	0.15	0.11	-	-	-	0.19
Sn	0.11	0.67	-	0.16	-	-	-	0.12	0.17	-
Bi	54.14	61.90	47.57	48.14	59.94	56.55	53.94	54.04	51.73	53.56
Te	7.65	12.15	3.03	12.15	3.54	6.15	7.42	8.45	9.99	8.97
Total	<b>9</b> 9.79			99.62	100.02	98.89	99.91	100.14	100.68	100.35

Formulae: 1. (Pd<sub>1.00</sub>Cu<sub>0.01</sub>)<sub>21.01</sub>(Bi<sub>0.78</sub> Te<sub>0.18</sub>Pb<sub>0.03</sub>Sb<sub>0.005</sub>Sn<sub>0.005</sub>)<sub>21.00</sub>

2.  $(Pd_{0.972}Pt_{0.003})_{\Sigma 0.975}(Bi_{0.67}Te_{0.28}Pb_{0.05})_{\Sigma 1.00}$ 

3.  $(Pd_{1.02}Pt_{0.01})_{\Sigma 1.03}(Bi_{0.89}Te_{0.15}Pb_{0.02})_{\Sigma 1.00}$ 

4. Pd<sub>1.00</sub>(Bi<sub>0.83</sub>Te<sub>0.15</sub>Pb<sub>0.02</sub>)<sub>Σ1.00</sub>

5.  $(Pd_{1.00}Zn_{0.01})_{\Sigma 1.01}(Bi_{0.78}Te_{0.17}Pb_{0.05})_{\Sigma 1.00}$ 

6.  $(Pd_{0.98}Cu_{0.01}Zn_{0.01})_{\Sigma 1.00}(Bi_{0.77}Te_{0.20}Pb_{0.03})_{\Sigma 1.00}$ 

7.  $(Pd_{1.02}Cu_{0.01})_{\Sigma 1.03}(Bi_{0.73}Te_{0.23}Pb_{0.03})_{\Sigma 1.00}$ 

8.  $(Pd_{1.01}Cu_{0.01})_{\Sigma 1.02}(Bi_{0.76}Te_{0.21}Pb_{0.02}Sb_{0.01})_{\Sigma 1.00}$ 

Column 1: mean composition (n = 47); columns 2-8 list representative compositions;

- indicates below minimum detection limit (0.05 wt.%).

	1 Mean	Max.	Min.	2	3
Pd wt.%	36.34	38.27	35.37	37.01	35.77
Pt	26.15	24,63	22.49	24.06	25.15
Cu	11.73	12.16	11.11	12.26	11.65
Zn	0.01	0.13	-	0.13	-
Sn	24.93	25.38	24.41	25.04	25.15
Bi	0.01	0.10	-	-	-
Te	0.49	0.36	0.14	0.18	0.36
Se	0.17	0.28	0.11	0.21	0.28
Total	97.84			98.89	98.36

TABLE 3. COMPOSITIONS OF "TAIMYRITE", NORIL'SK OREFIELD, RUSSIA

Formulae: 1.  $(Pd_{1.58} Cu_{0.85}Pt_{0.57})_{\Sigma 3.01} (Sn_{0.97}Te_{0.02}Se_{0.01})_{\Sigma 1.00}$ 

2.  $(Pd_{1,62}Cu_{0.90}Pt_{0.57}Zn_{0.01})_{\Sigma 3.10}(Sn_{0.98}Te_{0.01}Se_{0.01})_{\Sigma 1.00}$ 

3.  $(Pd_{1.54}Cu_{0.84}Pt_{0.59})_{\Sigma 2.97}(Sn_{0.97}Se_{0.02}Te_{0.01})_{\Sigma 1.00}$ 

Column 1: mean composition (n = 15); columns 2–3 list representative compositions.

- indicates below minimum detection limit (0.05 wt.%).

# Taimyrite

The analyzed phase (Pd, Pt)2.1Cu0.9Sn bears a close resemblance to taimyrite, [(Pd,Cu,Pt)<sub>3</sub>Sn; Begizov & Sluzhenikin (1976), Cabri (1976), Begizov et al. (1982); a revised formula,  $(Pd,Pt)_{9}Sn_{4}Cu_{3}$ , was given by Evstigneeva & Nekrasov (1984) for synthetic taimyrite], recently redefined as the Pd end-member of the taimyrite-tatyanaite solid-solution series (Barkov et al. 2000a, b). In fact, the mean composition, (Pd<sub>1.58</sub>Cu<sub>0.85</sub>  $Pt_{0.57}$ )  $\Sigma_{3.00}$  Sn, is nearly identical to that reported by Barkov et al. (2000a) from the Oktyabr' deposit (anal. 25 in their Table 3). However, the micro-analytical results are not sufficiently diagnostic by themselves, as taimyrite forms at least a partial solid-solution series with cabriite (Pd<sub>2</sub>CuSn; Evstigneeva & Genkin 1983), which it closely resembles both compositionally and structurally (Barkov et al. 2000a), and also with stannopalladinite [(Pd.Pt)<sub>5</sub>Sn<sub>2</sub>Cu: Evstigneeva & Nekrasov 1984]. X-ray data are needed to establish the identity of Pd-(Pt)-Cu stannides (the stannopalladinite group) and establish precise stoichiometry and compositional limits.

# Pt<sub>2</sub>FeCu (tulameenite?)

The composition  $Pt_2FeCu$  is identical to that given for tulameenite (Cabri *et al.* 1973), a mineral described from various placer deposits, from ultramafic rocks in the Tulameen Complex, British Columbia, in the Ural Mountains, and elsewhere, but to our knowledge, not previously reported from Noril'sk–Talnakh. The properties and paragenetic position of the  $Pt_2FeCu$  phase in this sample, in particular the occurrence as acicular and prismatic exsolved crystals in altaite, against which it displays a slight pink tint, are somewhat at odds with

> TABLE 4. COMPOSITIONS OF Pt<sub>2</sub>CuFe AND Pd(Bi,Pb), NORIL'SK OREFIELD, RUSSIA

	Pt <sub>z</sub> CuFe		Pd(	Bi,Pb)
	1	2	3	4
Pd wt.%	1.08	0.24	34.65	33.62
Pt	72.55	74.08	-	-
Ni	1.22	0.61	-	-
Cu	12.90	10.47	-	-
Fe	11.09	13.18		0.22
Pb	-	-	18.34	18.20
Sb	-	-	-	-
Sn	-	-	0.12	-
Bi	-	-	44.47	44.94
Те	-	-	0.23	0.14
Total	98.84	98.58	97.81	97.12

Formulae: 1. (Pt1.85Ni0.10 Pd0.05) 22.00Cu1.01Fe0.99

2.  $(Pt_{1.94}Ni_{0.05} Pd_{0.01})_{\Sigma 2.00}Cu_{0.84}Fe_{1.20}$ 

3. Pd<sub>1.07</sub>(Bi<sub>0.70</sub>Pb<sub>0.29</sub>Te<sub>0.01</sub>)<sub>Σ1.00</sub>

4.  $(Pd_{1.04}Fe_{0.01})_{\Sigma 1.05}(Bi_{0.71}Pb_{0.29}Te_{0.01})_{\Sigma 1.01}$ 

Note: - indicates below minimum detection limit (0.05 wt.%).

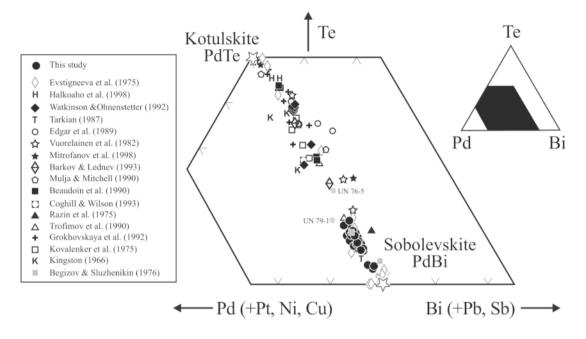


FIG. 4. Compositions of analyzed Pd(Te,Bi) phases plotted in Pd–Te–Bi space, compared to data in the original description of sobolevskite (Evstigneeva *et al.* 1975) and to other published compositional data for kotulskite and sobolevskite. UN–76–5 and UN–79–1 refer to compositions discussed by Cabri (1981b).

the original description of tulameenite (Cabri *et al.* 1973), in which altaite was not present. Cabri & Genkin (1991) noted that tulameenite is a secondary mineral formed during the serpentinization of ultramafic rocks, and usually found as a rim on primary platinum alloys, but that it occurs both in the lode deposits and within placers derived from such deposits. The occurrence in the present samples, exsolved at the margins of altaite–sobolevskite intergrowths, also contrasts with phase-equilibrium studies indicating crystallization directly from a magma (>1178°C) and "not by later processes at lower temperatures" (Shahmiri *et al.* 1985). The small size and intergrown character of the grains have not permitted extraction for a structural study to show conclusively that the Pt<sub>2</sub>FeCu phase is indeed tulameenite.

# Crystallization History, Textures, Exsolution and Paragenesis

The crystallization history of the assemblage is undeniably complex, and the large number of components (Pt–Pd–Bi–Te–Pb–Ag–Au–Sn–Cu–Fe–Ni–S–Te) precludes the application of phase equilibria within relatively simple binary or ternary systems, in which phase relationships are well constrained. Kovalenker *et al.* (1980) described subgraphic galena-rich segregations within massive ore from Talnakh–Oktyabr' as forming near-spherical bodies, some cm or tens of cm in size, in the upper parts of massive ore, close to the contact with gabbro dolerites. Temperatures as high as 820-840°C were invoked from the occurrence of glass formed by melting of minerals along the contact (Kovalenker et al. 1980). Conventional opinion has been that these spherical bodies, in which a wide variety of incompatible elements (PGE, together with Bi, Te, Pb, among others) are trapped, formed directly from a residual liquid. Phase relationships in the system Cu-Fe-Pb-S (Craig & Kullerud 1967, Toguzov et al. 1980) certainly suggest temperatures as high as 800°C for droplet-like unmixing of galena. Subsequent crystallization of intermediate solid-solution at ca. 600°C allowed droplets rich in exotic elements (Pt-Pd-Bi-Te-Ag-Au-Sn) to form. Evstigneeva (1989) attributed such assemblages to a temperature range of 450-200°C, arguing that some elements may have been supplied by hydrothermal solutions during post-magmatic transformations of the ore. Observed textures can thus be considered as the results of sequential exsolution as the ore continued to cool. Hydrothermal solutions, related to residual fluids, can also play a significant role in reconcentration in PGE deposits (e.g., Li & Naldrett 1993b), or remobilize PGE and other elements well after crystallization of sulfide and silicate magmas (e.g., Watkinson & Jones 1996). The association of PGM with chlorine-bearing phases

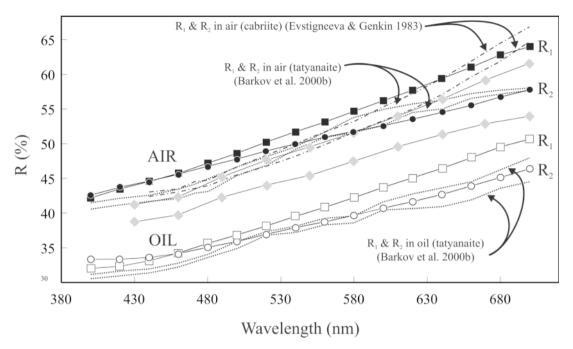


FIG. 5. Reflectance spectra for a taimyrite grain with the composition (Pt<sub>1.55</sub>Pd<sub>0.60</sub>Cu<sub>0.85</sub>)<sub>Σ3</sub>Sn in air (filled circle and square) and oil (white circle and square). For comparison: published reflectance data for taimyrite (grey diamonds; R<sub>1</sub> and R<sub>2</sub>; Begizov *et al.* 1982), tatyanaite (dotted lines; R<sub>1</sub> and R<sub>2</sub> in air and oil; Barkov *et al.* 2000b) and cabriite Pd<sub>2.04</sub>(Sn<sub>0.91</sub>Sb<sub>0.07</sub>)<sub>Σ0.98</sub>Cu<sub>0.98</sub> as broad dashed line (Evstigneeva & Genkin 1983).

has been used as indirect evidence for a late, relatively low-temperature (<400°C) genesis from late volatilerich fluids (*e.g.*, Li & Naldrett 1993b).

### CONCLUSIONS

Coarse symplectitic intergrowths of altaite and sobolevskite occur within a matrix of talnakhite in an assemblage displaying a complex history of exsolution as the ore cooled, either from magmatic temperatures, or from a later hydrothermal event. The textures reflect a protracted series of sequential unmixing and exsolution events. Extensive solid-solution along the kotulskite-sobolevskite join is documented, with broad variation in the ratio Bi/Te. An intermediate member of the taimyrite-tatyanaite series with a composition (Pd<sub>1.5</sub>  $Pt_{0.6}Cu_{0.85})_{\Sigma_3}Sn$  is a common component of such intergrowths, occurring at the margin of altaite-Pd(Bi,Te) symplectites. A Pt-Cu-Fe alloy occurs as small crystals at the outer margin of the altaite. This is probably the first report of a phase with the composition of tulameenite from Noril'sk.

#### ACKNOWLEDGEMENTS

The authors sincerely thank Drs. T.L. Evstigneeva and A.D. Genkin for assistance in obtaining some of the Russian references, for pertinent information and for discussion. The helpful comments of guest Associate Editor Andrei Barkov, two anonymous reviewers, and Robert F. Martin helped us improve this manuscript. This contribution is submitted for this special issue of *The Canadian Mineralogist* in recognition of Louis Cabri's outstanding achievements in the understanding the paragenesis and systematics of the platinum-groupminerals. Analytical work was carried out while the first author was at the Mineralogical Institute, University of Würzburg. P. Späthe is gratefully acknowledged for polishing the sample, and K.-P. Kelber, for assistance with photographs 2a and b.

### References

BARKOV, A.Y. & LEDNEV, A.I. (1993): A rhenium – molybdenum – copper sulfide from the Lukkulaisvaara layered intrusion, northern Karelia, Russia. *Eur. J. Mineral.* 5, 1227-1233.

- MARTIN, R.F., POIRIER G., TARKIAN, M., PAKHO-MOVSKII, Y.A. & MEN'SHIKOV. Y.P. (2000b): Tatyanaite, a new platinum-group mineral, the Pt analogue of taimyrite, from the Noril'sk complex (northern Siberia, Russia). *Eur. J. Mineral.* **12**, 391-396.
- \_\_\_\_\_, \_\_\_\_, \_\_\_\_ & YAKOVLEV, Y.N. (2000a): The taimyrite-tatyanaite series and zoning in intermetallic compounds of Pt, Pd, Cu, and Sn from Noril'sk, Siberia, Russia. *Can. Mineral.* 38, 599-609.
- BAYLISS, P. (1990): Revised unit-cell dimensions, space group, and chemical formula of some metallic minerals. *Can. Mineral.* 28, 751-755.
- BEAUDOIN, G., LAURENT, R. & OHNENSTETTER, D. (1990): First report of platinum-group minerals at Blue Lake, Labrador Trough, Quebec. *Can. Mineral.* 28, 409-418.
- BEGIZOV, V.D. & SLUZHENIKIN, S.F. (1976): On the compositions of some platinum minerals from the northwest and extreme north of the Talnakh ore junction. *Trudy TSNIGRI* 122, 107-112. (in Russ.).
- \_\_\_\_\_, ZAV'YALOV, E.N. & PALOV, E.G. (1982): New data on taimyrite (Pd,Cu,Pt)<sub>3</sub>Sn from copper–nickel ores of the Talnakh deposit. *Zap. Vses. Mineral. Obshch.* **111**, 78-83 (in Russ.).
- BERNHARDT, H.-J. (1987): A simple fully-automated system for ore mineral identification. *Mineral. Petrol.* 36, 241-245.
- BHATT, Y.C. & SCHUBERT, K. (1979): Kristallstruktur von PbBi. J. Less-Common Metals 64(2), 17-24.
- CABRI, L.J. (1976): New mineral names. Am. Mineral. 61, 180-181.
  - (1981a): The platinum-group minerals. In Platinum-Group Elements: Mineralogy, Geology, Recovery (L.J. Cabri, ed.). Can. Inst. Mining Metall., Spec. Vol. 23, 83-150.
- (1981b): Unnamed platinum-group minerals. In Platinum-Group Elements: Mineralogy, Geology, Recovery (L.J. Cabri, ed.). Can. Inst. Mining Metall., Spec. Vol. 23, 175-195.
- & GENKIN, A.D. (1991): Re-examination of Pt alloys from lode and placer deposits, Urals. *Can. Mineral.* **29**, 419-425.
- <u>& LAFLAMME, J.H.G. (1974):</u> Sudburyite, a new palladium–antimony mineral from Sudbury, Ontario. *Can. Mineral.* **12**, 275-279.
- \_\_\_\_\_ & \_\_\_\_ (1976): The mineralogy of the platinum-group elements from some copper-nickel deposits of the Sudbury area, Ontario. *Econ. Geol.* 71, 1159-1195.

Elements: Mineralogy, Geology, Recovery (L.J. Cabri, ed.). Can. Inst. Mining Metall., Spec. Vol. 23, 151-173.

- \_\_\_\_\_, OWENS, D.R. & LAFLAMME, J.H.G. (1973): Tulameenite, a new platinum – iron – copper mineral from placers in the Tulameen River area, British Columbia. *Can. Mineral.* 12, 21-25.
- COGHILL, B.M. & WILSON, A.H. (1993): Platinum-group minerals in the Selukwe Subchamber, Great Dyke, Zimbabwe: implications for PGE collection mechanisms and post-formational redistribution. *Mineral. Mag.* 57, 613-633.
- CRAIG, J.R. & KULLERUD, G. (1967): The Cu–Fe–Ni–S system. Carnegie Inst. Wash., Yearbook 65, 344-352.
- DISTLER, V.V., DYUZHIKOV, O.A. & GENKIN, A.D. (1993): The Talnakh ore field: a copper nickel platinum giant. *Geology of Ore Deposits* **35**, 1-13.
- & KUNILOV, V.E., eds. (1994): Geology and Ore Deposits of the Noril'sk Region. Seventh International Platinum Symposium (Moscow–Noril'sk), Field Trip Guidebook.
- DOBROVOL'SKAYA, M.G., MALOV, V.S. & VLADYKIN, N.V. (1985): Platinum and palladium minerals in charoitebearing rocks. *Dokl. Akad. Nauk SSSR, Earth Sci. Sect.* 284, 438-442.
- EDGAR, A.D., CHARBONNEAU, H.E. & MCHARDY, D.C. (1989): Pd bismuthotelluride minerals at Rathbun Lake, Ontario: significance to post-magmatic evolution of PGE deposits. *Neues Jahrb. Mineral.*, *Monatsh.*, 461-475.
- EVSTIGNEEVA, T.L. (1989): Noble metal mineralization and its position in the process of the Cu–Ni sulfide ore formation. *Bull. Geol. Soc. Finland* **61**, 34 (abstr.).
- & GENKIN, A.D. (1983): Cabriite Pd<sub>2</sub>SnCu, a new species in the mineral group of palladium, tin and copper compounds. *Can. Mineral.* 21, 481-487.
- \_\_\_\_\_ & \_\_\_\_\_ (1990): Some problems of PGM nomenclature. In Problems of Genetic and Applied Mineralogy (S.V. Malinko & E.I. Semenov, eds.). Nauka, Moscow, Russia (196-209; in Russ.).
- \_\_\_\_\_\_ & KOVALENKER, V.A. (1976): Sobolevskite, a new bismuthide of palladium, sobolevskite, and the nomenclature of minerals of the system PdBi–PdTe– PdSb. Int. Geol. Rev. 18, 856-866.
- & NEKRASOV, N.Y. (1984): Conditions of formation of tin-bearing platinum-group minerals in the system Pd– Cu–Sn and its partial cross sections. *In* Tin in Magmatic and Postmagmatic Processes (N.Y. Nekrasov, ed.). Nauka, Moscow, Russia (143-170; in Russ.).
- FARROW, C.E.G. & WATKINSON, D.H. (1997): Diversity of precious-metal mineralization in footwall Cu–Ni–PGE deposits, Sudbury, Ontario: implications for hydrothermal models of formation. *Can. Mineral.* 35, 817-839.

- GENKIN, A.D. (1968): Minerals of the Platinum Metals and their Associations in the Copper–Nickel Ores of Noril'sk Deposit. Nauka, Moscow, Russia (in Russ.).
  - , DISTLER, V.V., GLADYSHEV, G.D., FILIMONOVA, A.A., EVSTIGNEEVA, T.L., KOVALENKER, V.A., LUPUTINA, I.P., SMIRNOV, A.V. & GROKHOVSKAYA, T.L. (1981): Sulfide Copper–Nickel Ores of Noril'sk Deposits. Nauka, Moscow, Russia (in Russ.).
  - & EVSTIGNEEVA, T.L. (1986): Associations of platinum-group minerals of the Noril'sk copper–nickel sulphide ores. *Econ. Geol.* 81,1203-1212.
  - \_\_\_\_\_, \_\_\_\_, TRONEVA, N.V. & VYAL'SOV, L.N. (1969): Polarite Pd(Pb,Bi); a new mineral of copper–nickel sulfide ores. *Zap. Vses. Mineral. Obshchest.* **98**, 708-715 (in Russ.).
  - \_\_\_\_\_, \_\_\_\_, VYAL'SOV, L.N., LAPUTINA, I.P. & TRONEVA, N.V. (1975): Paolovite, Pd<sub>2</sub>Sn, a new mineral from copper–nickel sulfide ores. *Int. Geol. Rev.* 17, 342-346.
- \_\_\_\_\_, ZHURAVLEV, N.N. & SMIRNOVA, E.M. (1963): Moncheite and kotulskite – new minerals – and the composition of michenerite. *Zap. Vses. Mineral. Obshchest.* 92, 33-50 (in Russ.).
- GROKHOVSKAYA, T.L., DISTLER, V.V., KLYUNIN, S.F., ZAKHAROV, A.A. & LAPUTINA, I.P. (1992): Low-sulfide platinum group mineralization of the Lukkulaisvaara Pluton, northern Karelia. *Int. Geol. Rev.* 34, 503-520.
- HALKOAHO, T., ABZALOV, M. & PAPUNEN, H. (1998): Platinumgroup minerals in the lower layered unit of the Pana Tundra layered intrusion on the Kola Peninsula. *In* International Platinum (N.P. Laverov V.V. Distler, eds.). Theophrastus, St. Petersburg, Russia (54-61).
- KINGSTON, G.A. (1966): the occurrence of platinoid bismuthotellurides in the Merensky Reef at Rustenburg platinum mine in the western Bushveld. *Mineral. Mag.* 35, 815-834.
- KOVALENKER, V.A., GENKIN, A.D., YEVSTIGNEEVA, T.L. & LAPUTINA, I.P. (1975): Telargpalite, a new mineral of palladium, silver and tellurium from the copper–nickel ores of the Oktyabr' deposit. *Int. Geol. Rev.* 17, 817-822.
  - \_\_\_\_\_, LAPUTINA, I.P., VYAL'SOV, L.N., GENKIN, A.D. & YEVSTIGNEEVA, T.L. (1973): Tellurium minerals in coppernickel sulfide ores at Talnakh and Oktyabr' (Noril'sk district). *Int. Geol. Rev.* **15**, 1284-1294.
- \_\_\_\_\_\_& PAVLOV, E.G. (1980): On the exsolution of the natural solid solution in the system PbS– PbTe. *In* Ordering and Decomposition of Solid Solutions in Minerals, Nauka, Moscow, Russia (185-190; in Russ.).
- LI, CHUSI & NALDRETT, A.J. (1993a): Platinum-group minerals from the Deep Copper Zone of the Strathcona deposit, Sudbury, Ontario. *Can. Mineral.* 31, 31-44.
  - \_\_\_\_\_ & \_\_\_\_\_ (1993b): High chlorine alteration minerals and calcium-rich brines in fluid inclusions from

the Strathcona Deep Copper Zone, Sudbury, Ontario. Econ. Geol. 88, 1780-1796.

- MARCHETTO, C.M.L. (1990): Platinum-group minerals in the O'Toole (Ni–Cu–Co) deposit, Brazil. *Econ. Geol.* 85, 921-927.
- MITROFANOV, F.P., BALABONIN, N.L., KORCHAGIN, A.U., BAYANOVA, T.B., LATYPOV, R.M., GONCHAROV, Y.V., OSOKIN, A.S. & GRITSAI, A.L. (1998): PGE mineralization of the Fedorova – Pansky intrusion (Kola Peninsula, Russia). *In* International Platinum (N.P. Laverov & V.V. Distler, eds.). Theophrastus, St. Petersburg, Russia (62-70).
- MULJA, T. & MITCHELL, R.H. (1990): Platinum-group minerals and tellurides from the Geordie Lake intrusion, Coldwell complex, northwestern Ontario. *Can. Mineral.* 28, 489-501.
- RAZIN, L.V., BEGIZOV, V.D. & MESHCHANKINA, V.I. (1975): Data on mineralogy of platinum metals in the Talnakh deposit. *Int. Geol. Rev.* 17, 6-56.
- RUDASHEVSKY, N.S., AVDONTSEV, S.N. & DNEPROVSKAYA, M.B. (1992): Evolution of PGE mineralization in hortonolitic dunites of the Mooihoek and Onverwacht pipes, Bushveld Complex. *Mineral. Petrol.* 47, 37-54.
- SHAHMIRI, M., MURPHY, S. & VAUGHAN, D.J. (1985): Structural and phase equilibria studies in the system Pt–Fe–Cu and the occurrence of tulameenite (Pt<sub>2</sub>FeCu). *Mineral. Mag.* 49, 547-554.
- SHVEDOV, G.I., TOLSTYKH, N.D., NEKOS, V.V. & POSPELOVA, L.N. (1997): Minerals of platinum group in sulfide Cu–Ni ores of the Kingash Massif (East Sayan). *Russ. Geol. Geophys.* 38, 1872-1878.
- STUMPFL, E.F. & TARKIAN, M. (1976): Platinum genesis: new mineralogical evidence. *Econ. Geol.* 71, 1451-1460.
- TARKIAN, M. (1987): Compositional variations and reflectance of the common platinum-group minerals. *Mineral. Petrol.* 36, 169-190.
- TOGUZOV, M.Z., KOPYLOV, N.I. & SYCHEV, A.P. (1980): The Cu<sub>2-x</sub>S-FeS-PbS-ZnS system. *Russ. J. Inorg. Chem.* 25, 1239-1241.
- TOLSTYKH, N.D., KRIVENKO, A.P., PAL'CHIK, N.A. & IZOKH, A.E. (1997): New Sb- and Te-containing varieties of sobolevskite PdBi. Dokl. Russ. Acad. Sci., Earth Sci. Sect. 357, 1145-1148.
- TROFIMOV, N.N., BARKOV, A.Y., LEDNEV, A.I., LAVROV, M.M. & GANIN, V.A. (1990): The first data on minerals of platinum-group metals in the Burakovsky layered complex (Karelia). Dokl. Akad. Nauk SSSR 315, 703-706 (in Russ.).
- TVRDÝ, J. & KOLESAR, P. (1995): Noril'sk die schwarze Perle Nordsibiens. Lapis 20, 13-32.
- VUOROELAINEN, Y., HÄKLI, T.A., HÄNNINEN, E., PAPUNEN, H., REINO, J. & TÖRNROOS, R. (1982): Isomertierite and other

platinum-group minerals from the Konttijärvi layered mafic intrusion, northern Finland. *Econ. Geol.* **77**, 1511-1518.

- WATKINSON, D.H. & JONES, P.C. (1996): Platinum-group minerals in fluid inclusions from the Marathon deposit, Coldwell Complex, Canada. *Mineral. Petrol.* 57, 91-96.
  - & OHNENSTETTER, D. (1992): Hydrothermal origin of platinum-group mineralization in the Two Duck Lake intrusion, Coldwell Complex, northwestern Ontario. *Can. Mineral.* **30**, 121-136.
- YAKOVLEV, Y.N., DISTLER, V.V., MITROFANOV, F.P., RAZHEV, S.A., GROKHOVSKAYA, T.L. & VESELLOVSKY, N.N. (1991): Mineralogy of PGE in the mafic–ultramafic massifs of the Kola Region. *Mineral. Petrol.* **43**, 181-192.
- YUSHKO-ZAKHAROVA, O.Y., MALEVSKIY, A.Y. & DUBAKINA, L.S. (1974): Lead–bismuth isomorphism in palladium-rich minerals in the system Pd–Pb–Bi. *Geochem. Int.* **11**, 1133-1138.
- Received May 19, 2001, revised manuscript accepted February 23, 2002.