

## TÖRNROOSITE, $Pd_{11}As_2Te_2$ , A NEW MINERAL SPECIES RELATED TO ISOMERTIEITE FROM MIESSIJOKI, FINNISH LAPLAND, FINLAND

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### ABSTRACT

Törnroosite, ideally  $Pd_{11}As_2Te_2$ , is a new mineral species discovered in a heavy-mineral concentrate from the Miessijoki River, Lemmenjoki area, Inari Commune, Finnish Lapland, Finland. It is cubic, space group  $Fd\bar{3}m$  (#227), by analogy with isomertieite,  $a$  12.3530(4) Å,  $V$  1885.03 (1) Å<sup>3</sup>,  $Z$  = 8. The strongest six lines of the X-ray powder-diffraction pattern [ $d$  in Å (I)  $hkl$ ] are: 2.182(100)440, 2.376(90)511, 333, 1.544(15)800, 1.862(13)622, 1.2606(13)844, and 1.608(11)731, 553. The associated minerals include sperrylite, Pt–Fe alloy, cooperite, braggite, native Os–Ir–Ru alloy, irarsite, laurite, isomertieite, mertieite II, native Pt, native gold–silver alloy, atokite, Pt–Cu alloy, Cu–Pt–Pd alloy, Cu–Pd–Pt–Au alloy, Pd–Au alloy, along with magnetite, ilmenite, chromite, columbite–tantalite, tapiolite, garnet, monazite, zircon, pyrite, rutile, uraninite–thorianite, galena, and a mineral of the wolframite series. Törnroosite is black, opaque with a metallic luster, with a silvery black streak. The mineral is isotropic with a yellowish white color in comparison with sperrylite. The reflectance values in air for the standard COM wavelengths are: 45.4 (470 nm), 51.0 (546 nm), 54.1 (589 nm) and 57.45% (650 nm). The calculated density is 11.205(1) g/cm<sup>3</sup> (for the empirical formula and unit-cell parameter refined from powder data). The electron-microprobe analyses gave, on average, Pd 72.04, Pt 1.75, Sn 2.13, Sb 0.85, As 8.77, Te 13.15 and Bi 0.79, total 99.48 wt.%, which corresponds to  $(Pd_{10.85}Pt_{0.14})_{\Sigma 10.99}(As_{1.88}Sb_{0.11})_{\Sigma 1.99}(Te_{1.65}Sn_{0.29}Bi_{0.06})_{\Sigma 2.00}$ , based on a total of 15 atoms per formula unit. The average micro-indentation hardness (VHN<sub>25</sub>) is 519 ( $n$  = 4), corresponding to a Mohs hardness of 5. The mineral is named after Professor Ragnar Törnroos, University of Helsinki, Finland.

**Keywords:** törnroosite, new mineral species, isomertieite structure, palladium arsenotelluride, X-ray data, electron-microprobe data, reflectance, hardness, Miessijoki River, Lemmenjoki area, Finland.

### SOMMAIRE

La törnroosite, de composition idéale  $Pd_{11}As_2Te_2$ , est une nouvelle espèce minérale découverte dans un concentré de minéraux denses prélevé dans la rivière Miessijoki, région de Lemmenjoki, commune d’Inari, Laponie finlandaise, Finlande. Il s’agit d’un minéral cubique, groupe spatial  $Fd\bar{3}m$  (#227) par analogie à l’isomertieïte,  $a$  12.3530(4) Å,  $V$  1885.03 (1) Å<sup>3</sup>,  $Z$  = 8. Les six raies les plus intenses du spectre de diffraction, méthode des poudres [ $d$  en Å (I)  $hkl$ ] sont: 2.182(100)440, 2.376(90)511, 333, 1.544(15)800, 1.862(13)622, 1.2606(13)844, et 1.608(11)731, 553. Lui sont associés sperrylite, alliage Pt–Fe, cooperite, braggite, alliage Os–Ir–Ru, irarsite, laurite, isomertieïte, mertieïte II, Pt natif, alliage d’or et d’argent, atokite, alliage Pt–Cu, alliage Cu–Pt–Pd, alliage Cu–Pd–Pt–Au, alliage Pd–Au, ainsi que magnétite, ilménite, chromite, hématite, columbite–tantalite, tapiolite, grenat, monazite, zircon, pyrite, rutile, uraninite–thorianite, galène, et un minéral de la série de la wolframite. La törnroosite est noire, opaque avec un éclat métallique, et une rayure noir argenté. Le minéral est isotrope avec une couleur blanc jaunâtre en comparaison avec la sperrylite. Les valeurs de réflectance dans l’air pour les longueurs d’onde standard COM sont: 45.4 (470

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nm), 51.0 (546 nm), 54.1 (589 nm) and 57.45% (650 nm). La densité calculée est 11.205(1) g/cm<sup>3</sup> (pour la formule empirique et le paramètre réticulaire affiné à partir des données en diffraction X acquises sur poudre). Les analyses effectuées avec une microsonde électronique ont donné, en moyenne, Pd 72.04, Pt 1.75, Sn 2.13, Sb 0.85, As 8.77, Te 13.15 et Bi 0.79, pour un total de 99.48% (poids), ce qui correspond à  $(\text{Pd}_{10.85}\text{Pt}_{0.14})_{\Sigma 10.99}(\text{As}_{1.88}\text{Sb}_{0.11})_{\Sigma 1.99}(\text{Te}_{1.65}\text{Sn}_{0.29}\text{Bi}_{0.06})_{\Sigma 2.00}$ , sur une base de 15 atomes par unité formulaire. La dureté mesurée par micro-indentation (VHN<sub>25</sub>) est 519 ( $n = 4$ ), ce qui correspond à une dureté de Mohs de 5. Le minéral honore le professeur Ragnar Törnroos, de l'université de Helsinki, en Finlande.

**Mots-clés:** törnroosite, nouvelle espèce minérale, structure de l'isomertieite, arsénottellurure de palladium, diffraction X, données de microsonde électronique, réflectance, dureté, rivière Miessijoki, région de Lemmenjoki, Finlande.

## INTRODUCTION

Törnroosite, ideally  $\text{Pd}_{11}\text{As}_2\text{Te}_2$ , was discovered in a polished section of a platinum-group mineral (PGM) separate obtained in the summer of 2005 from the Miessijoki River, Finnish Lapland, courtesy of Mr. Pekka Turkka. A single grain of törnroosite, measuring 130 × 200 µm in size, was found during an electron-microprobe study of the PGM conducted at the Geological Survey of Finland. The mineral is named after Professor Ragnar Törnroos (*b.* 1943), University of Helsinki, who first called attention to a mineral of similar composition (Törnroos *et al.* 1996). Prof. Törnroos has been involved for many years in pioneering research work on the placer PGM in the Ivalojoki and Lemmenjoki tributaries in Finnish Lapland. A total of 43 PGE-bearing minerals or native metal alloys have been identified by him and his coworkers. The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names, IMA (2010–043). The holotype, specimen number BM 2010,100, is stored in the Natural History Museum, Cromwell Road, SW7 5BD, U.K.

Our purpose in this paper is to describe the physical and chemical attributes of törnroosite.

## THE TYPE LOCALITY

Törnroosite was discovered along with placer gold and PGM nuggets in the glaciofluvial gravels and sands of the Miessijoki River in the Lemmenjoki area, Inari commune, Finnish Lapland, Finland (Fig. 1). The discovery locality is at longitude 25°42'33"N and latitude 68°42'30"E. The PGM exist as individual grains or as inclusions and exsolution lamellae in larger grains PGM (Kojonen *et al.* 2006a, 2006b). The bedrock in the area is *ca.* 2.1 Ga old Proterozoic granulite (Meriläinen 1976, Tuisku & Huhma 2003) of probable sedimentary origin, containing felsic pegmatite and quartz–carbonate veins, along with pyroxene gabbro, the latter likely from an unidentified layered intrusion. The granulite complex of northern Finland forms an arc that extends from the Norwegian border in the west to the Russian border in the east. This arc is bordered to the southwest by greenstones, mafic and ultramafic intrusions, along with mica–quartz–feldspar schists and gneisses.

The sources of the placer gold, PGM, minerals of the columbite–tantalite series and tapiolite are not

known. However, the most probable sources for gold are the quartz–carbonate veins, for the PGM, the mafic–ultramafic intrusions, and for the columbite–tantalite, complex granitic pegmatites, respectively. The area occurs in the Lemmenjoki National Park, where no extensive exploration drilling is allowed.

## SAMPLES AND METHODS OF INVESTIGATION

Magnetite was removed with a strong hand-held magnet from the black sand heavy-mineral concentrate, and coarse-grained PGM were picked up under a stereo microscope. The black sand consists of titaniferous magnetite, ilmenite, chromite, hematite, columbite–tantalite, tapiolite, garnet, monazite, zircon, pyrite, rutile, uraninite–thorianite, galena, and minerals of the wolframite series. The coarse PGM fraction of the sample was found to contain 56 grains of Pt–Fe alloy, 40 grains of sperrylite, three grains of mertieite or isomertieite, three grains of cooperite, one grain of atokite, two grains of Os–Ir–Ru alloy, 10 grains of Pt–Cu alloy, six grains of Pd–Cu–Au alloy, six grains of Pd–Au alloy, one grain of arsenopyrite, one grain of titaniferous magnetite, one grain of ilmenite, and one grain of pyrite. The Pt–Fe alloy contains inclusions of laurite, irarsite, hollingworthite, and cuproiridsite. Fine-grained PGM grains were mounted in a SEM specimen holder 10 mm in diameter and examined with a JEOL JSM 5900 LV scanning electron microscope with energy-dispersion spectrometry employing an Oxford Instruments INCA automatic FEATURE ANALYSIS program to define the PGM phases and their grain sizes. Törnroosite is associated with 2,942 grains of sperrylite, 25 grains of mertieite or isomertieite, and five grains of cooperite or braggite. The lighter oxides and sulfides still present in the specimen were segmented out in the BSE images during the automatic FEATURE ANALYSIS runs. Subsequently, the PGM grains were mounted in epoxy, and those differing in color from the sperrylite grains and those showing optical anisotropism under polarized light were analyzed with a Cameca SX–100 electron microprobe at the Geological Survey of Finland. A single grain of törnroosite (Fig. 2) was discovered in a polished specimen prepared from the PGM fine size-fraction. The micro-indentation Vickers Hardness Number (VHN) was measured with a Leitz Duriment hardness tester, and reflectance values were

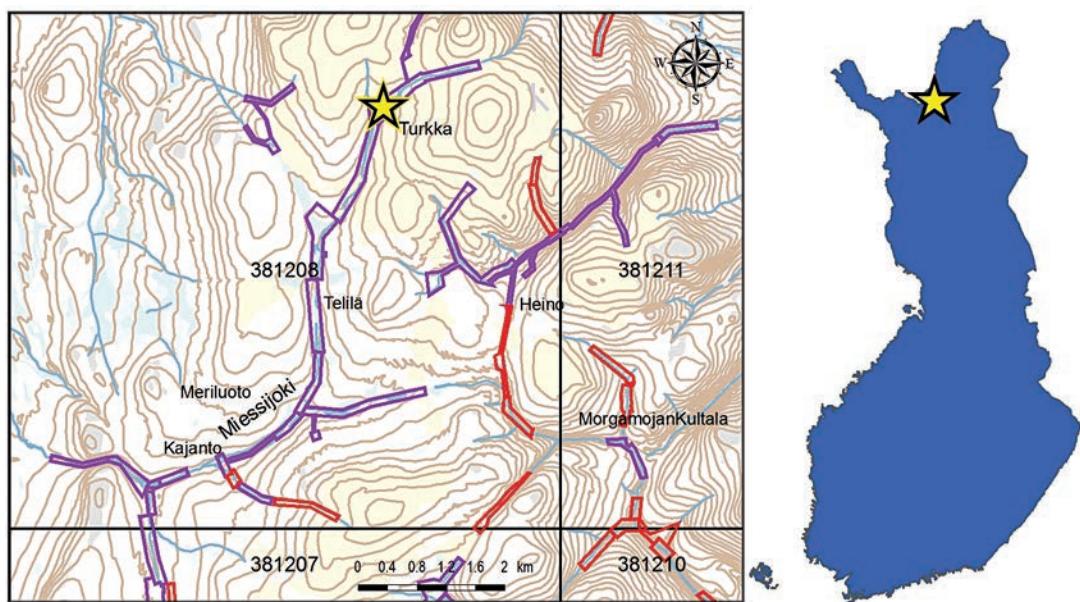


FIG. 1. Map showing the discovery location (star) of törnroosite in the Miessijoki River, Finland. The outlined areas along river valleys are gold claims and mining concessions. Map by Geological Survey of Finland, Active Map Explorer ©. Map drawn by Ms. Kirsti Keskisaari.

measured with a Zeiss Axiotron polarizing microscope equipped with a JM Tidas diode array spectrometer, a 20 $\times$  measuring objective, a 100 W halogen light source, with WTIC (Zeiss #314) being used as a standard. The estimated area of measurement was 20  $\times$  20  $\mu\text{m}$ .

#### OPTICAL, PHYSICAL, CRYSTALLOGRAPHIC AND CHEMICAL PROPERTIES

##### *Optical properties*

Törnroosite is macroscopically opaque with a metallic luster. The streak is black to silvery black. Under plane-polarized reflected light in air, törnroosite is yellowish white and under crossed polarizers, it is isotropic. The grain is anhedral (Fig. 2) and has an irregular fracture. The reflectance values are shown in Table 1, and a reflectance curve is shown in Figure 3. The values for the COM standard wavelengths 470, 546, 589 and 650 nm were calculated. The calculated CIE color values and the dominant wavelength also are given in Table 1.

##### *Physical properties*

Only one grain of törnroosite, measuring 132  $\times$  200  $\mu\text{m}$ , has been discovered. The Vickers Hardness Number was measured with a 25 g load, resulting in perfect or slightly fractured indentations that range from

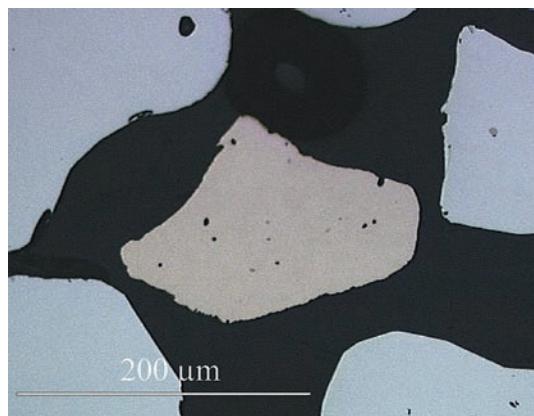


FIG. 2. Grain of törnroosite (yellowish white) with sperrylite grains (white) in polished section. Plane-polarized reflected light, sample Turkka 2005, Miessijoki.

509 to 536 with an average of 519, corresponding to a Mohs hardness of 5. The calculated density is 11.205(1)  $\text{g}/\text{cm}^3$ , based on the average empirical formula derived from the electron-microprobe analyses and the unit-cell parameter refined from the X-ray powder-diffraction data.

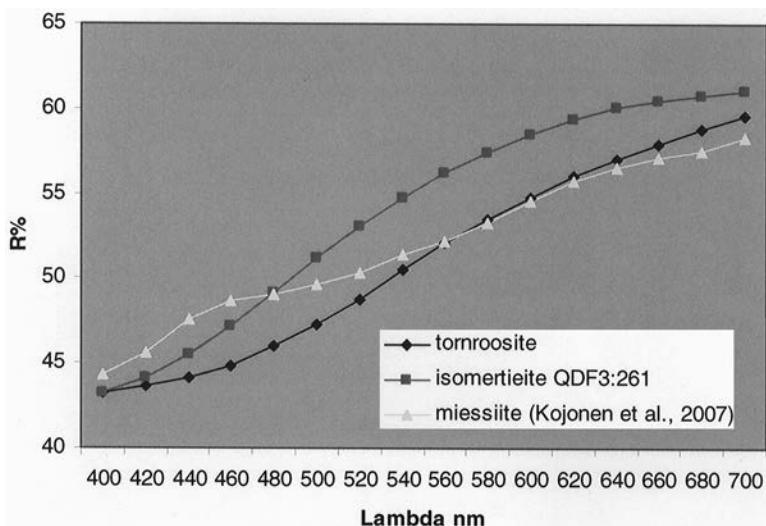


FIG. 3. Reflectance spectra for törnroosite, isomertieite and miessiite (Criddle & Stanley 1993, Kojonen *et al.* 2007).

TABLE 1. REFLECTANCE AND COLOR VALUES FOR TÖRNROOSITE, ISOMERTIEITE AND MIESSIITE

$\lambda$	Trs			Ism			Mie		
	R	R	R	$\lambda$	R	R	R		
400 nm	43.2%	43.2%	44.3%	560 nm	52.1%	56.2%	52.2%		
420	43.6	44.1	45.65	580	53.5	57.4	53.3		
440	44.1	45.5	47.6	589	54.1	57.9	53.9		
460	44.8	47.2	48.65	600	54.8	58.55	54.6		
470	45.4	48.2	48.9	620	56.0	59.4	55.7		
480	46.0	49.15	49.1	640	57.0	60.1	56.5		
500	47.3	51.2	49.6	650	57.45	60.3	56.8		
520	48.8	53.1	50.3	660	57.9	60.5	57.1		
540	50.5	54.75	51.4	680	58.8	60.8	57.55		
560	51.0	55.2	51.6	700	59.6	61.1	58.3		

#### Color values C illuminant

x	0.329	0.330	0.322
y	0.332	0.336	0.325
$\gamma\%$	51.7	55.6	53.2
$\lambda_d$	580	578	582
Pe%	9.3	10.5	5.9

Isomertieite data from QDF3: 261, Criddle & Stanley (2003); miessiite data from Kojonen *et al.* (2007), sample Turkka fine fraction 2005 (Fig. 2). Symbols used: Trs: törnroosite, Ism: isomertieite, Mie: miessiite.

#### X-ray crystallography

A small portion of the törnroosite grain ( $\sim 35 \mu\text{m}$ ) was excavated from the polished section (Fig. 2) using a razor blade. The grain was affixed to a tapered glass

filament (diameter  $\sim 15 \mu\text{m}$ ) using five-minute epoxy and mounted in a 114.6-mm-diameter Gandolfi camera. The X-ray-diffraction data were collected with a Philips PW 1870 X-ray generator operating at 40 kV and 30 mA, using a 0.3 mm collimator, a 72-hour exposure, an image plate and Ni-filtered  $\text{CuK}\alpha_{\text{avg}}$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The image plate was scanned and an integrated diffractogram calculated using the program DIIS (Petrus *et al.*, submitted). Individual peak positions were determined based on  $\text{CuK}\alpha_1$  (calculated assuming an  $\alpha_1:\alpha_2$  ratio of 0.5) and intensities normalized to the measured intensity of  $d = 2.182 \text{ \AA}$  ( $I = 100$ ), using the software package X'PERT HIGHSCORE PLUS Ver. 2.2.0 (Panalytical 2006). Indexing of reflections and space-group assignment were by analogy with isomertieite, given the strong similarity in their X-ray-diffraction patterns. By analogy with isomertieite, törnroosite is cubic, space group is  $F\bar{d}3m$ ,  $a = 12.3530(4) \text{ \AA}$ ,  $V = 1885.03(1) \text{ \AA}^3$  and  $Z = 8$  (McDonald & Cabri 2005). Data pertaining to the complete X-ray powder-diffraction pattern are given in Table 2. Additional diffraction lines at 7.20  $\text{\AA}$  ( $I = 25$ ), 6.61 ( $I < 5$ ) and 2.98 ( $I = 5$ )  $\text{\AA}$ , inconsistent with published X-ray patterns for isomertieite, were also noted. Kaolinite was observed in the original material that was collected, and this could explain the line at 7.20  $\text{\AA}$ . However, the source of the other two lines is not clear; they are conditionally attributed to an unidentified, associated mineral(s). Törnroosite is isostructural with isomertieite ( $\text{Pd}_{11}\text{As}_2\text{Sb}_2$ ) and miessiite ( $\text{Pd}_{11}\text{Se}_2\text{Te}_2$ ) and can thus be assigned to the Nickel-Strunz class 2.AC.15 (Strunz & Nickel 2001), alloys of metalloids with PGE. The Pearson Symbol Code is *cF* 120.

### Chemical composition

Quantitative electron-microprobe analyses of törnroosite were performed using a Cameca SX-100 electron microprobe, with an operating voltage of 15 kV, a beam current of 20 nA, and a beam-spot diameter of 3 µm. We used as standards metallic Pd for Pd, sperrylite for Pt, cassiterite for Sn, cobaltite for As, Sb<sub>2</sub>Te<sub>3</sub> for Sb and Te. In addition, Rh, Ag, Cu, Ni, Co, Se and S were sought but not detected. The measurement times, peaks and analyzing crystals were: for Pd, 20 s on Pd  $\text{M}\alpha_1$  and LPET, for Pt, 15 s, Pt  $\text{L}\alpha_1$  and LLIF, for As, 20 s, As  $\text{L}\alpha_1$  and TAP, for S, K $\alpha_1$  and PET, for Sn, 20 s, Sn $\text{L}\alpha_1$  and LPET, for Sb, 30 s and Sb $\text{L}\alpha_1$  and PET, for Te, 30 s, Te $\text{L}\alpha_1$  and LLIF, respectively. The background

was measured for 10 s, except for Pt, Te and Sb, where they were measured for 15 s. The average result of 10 analyses is Pd 72.04, Pt 1.75, Sn 2.13, Sb 0.85, As 8.77, Te 13.15, Bi 0.79, total 99.48 wt.%, corresponding to  $(\text{Pd}_{0.85}\text{Pt}_{0.14})_{\Sigma 10.99}(\text{As}_{1.88}\text{Sb}_{0.11})_{\Sigma 1.99}(\text{Te}_{1.65}\text{Sn}_{0.29}\text{Bi}_{0.06})_{\Sigma 2.00}$  (Table 3) based on a total of 15 atoms *pfu*. The idealized formula is Pd<sub>11</sub>As<sub>2</sub>Te<sub>2</sub>, which requires Pd 74.29, As 9.51, Te 16.20, total 100.00 wt.% (Table 4). In addition, published results of three analyses of a similar mineral from the Bushveld complex (Oberthür *et al.* 2005), and of seven analyses of this study (Table 4) are very similar, suggesting the mineral may well also occur in the Bushveld Complex. However, confirmation of törnroosite still requires crystal-structure verification (*e.g.*, via X-ray powder-diffraction analysis). In terms of the compositions obtained, törnroosite generally exhibits a higher content of Sn and Pt and a lower content of Pd and Te, relative to the mineral from the Bushveld. In analysis 2 from Bushveld, Sb and As contents are higher but Te lower compared with the törnroosite compositions.

### DISCUSSION

Törnroosite, characterized as a new mineral species with the ideal composition Pd<sub>11</sub>As<sub>2</sub>Te<sub>2</sub>, is cubic, space group  $Fd\bar{3}m$ , and with a unit-cell parameter *a* refined from powder data equal to 12.3530(4) Å. On the basis of the Gandolfi X-ray pattern obtained, törnroosite is considered to be isostructural with isomertieite and miessite. Comparative data for törnroosite, isomertieite and miessite are shown in Tables 1, 5 and 6. All are cubic, space group  $Fd\bar{3}m$ , with the lattice constant *a* varying only slightly: it is smallest in isomertieite, intermediate in törnroosite and largest in miessite. Törnroosite is a Pd telluride, with Te substituting for Sb in isomertieite. All three of these minerals occur in the placers of the Miessijoki River, suggesting a common origin. The empirical formula, based on the average

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR TÖRNROOSITE

<i>I</i> <sub>obs</sub>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>h k l</i>
3	3.713	3.725	3 1 1
2	3.561	3.566	2 2 2
1	2.827	2.834	3 3 1
11	<b>2.519</b>	<b>2.526</b>	<b>4 2 2</b>
90	<b>2.376</b>	<b>2.377</b>	<b>5 1 1, 3 3 3</b>
100	<b>2.182</b>	<b>2.184</b>	<b>4 4 0</b>
8	2.058	2.059	4 4 2
4	1.953	1.953	6 2 0
4	1.883	1.884	5 3 3
13	<b>1.862</b>	<b>1.862</b>	<b>6 2 2</b>
5	1.729	1.730	7 1 1
1	1.650	1.651	6 4 2
11	<b>1.608</b>	<b>1.608</b>	<b>7 3 1, 5 5 3</b>
14	<b>1.544</b>	<b>1.544</b>	<b>8 0 0</b>
10	1.4554	1.4558	6 6 0, 8 2 2
4	1.4166	1.4170	5 5 5, 6 6 2
5	1.3475	1.3478	8 4 2
10	1.2947	1.2949	9 3 1
13	<b>1.2606</b>	<b>1.2608</b>	<b>8 4 4</b>
6	1.2412	1.2415	9 3 3, 7 5 5
1	1.2110	1.2113	10 2 0
8	1.1942	1.1942	9 5 1, 10 2 2
2	1.1520	1.1519	9 5 3
4	1.0920	1.0919	8 8 0
2	1.0758	1.0752	10 4 4
1	1.0444	1.0440	10 6 2
1	1.0190	1.0189	11 5 1
4	1.0021	1.0020	10 6 4
2	0.9768	0.9766	12 4 0
1	0.9678	0.9676	9 9 1
3	0.9421	0.9419	10 6 6
3	0.9234	0.9233	11 7 3
3	0.9107	0.9107	12 6 2
6	0.9034	0.9033	9 9 5
7	0.8846	0.8846	13 5 1, 11 7 5
5	0.8734	0.8735	14 2 0, 10 10 0
9	0.8648	0.8649	14 2 2
1	0.8404	0.8405	14 4 2
7	0.8347	0.8347	13 7 1
11	<b>0.8253</b>	<b>0.8254</b>	<b>12 8 4</b>
2	0.8198	0.8199	13 7 3, 11 9 5
3	0.8108	0.8110	14 6 0
11	0.8039	0.8041	14 6 2
6	0.7922	0.7924	11 11 1, 15 3 3
4	0.7841	0.7844	14 6 4
5	0.7794	0.7797	13 9 1
1	0.7770	0.7766	12 10 3

Values of *d* are expressed in Å.

TABLE 3. AVERAGE ELECTRON-MICROPROBE DATA FOR TÖRNROOSITE

	average <i>n</i> = 10	range	Standard deviation	Microprobe standard
Pd wt.%	72.04	71.47 – 72.79	0.50	Pd
Pt	1.75	1.61 – 1.90	0.10	sperrylite
Sn	2.13	2.08 – 2.20	0.04	cassiterite
Sb	0.85	0.81 – 0.89	0.04	Sb <sub>2</sub> Te <sub>3</sub>
Bi	0.79	0.70 – 0.89	0.06	Bi
As	8.77	8.63 – 8.89	0.08	cobaltite
Te	13.15	12.76 – 13.56	0.25	Sb <sub>2</sub> Te <sub>3</sub>
Total	99.48			

Cameca SX-100 electron microprobe, accelerating voltage 10 kV, beam current 20 nA, beam diameter 3 µm.

Empirical formula:  $(\text{Pd}_{0.85}\text{Pt}_{0.14})_{\Sigma 10.99}(\text{As}_{1.88}\text{Sb}_{0.11})_{\Sigma 1.99}(\text{Te}_{1.65}\text{Sn}_{0.25}\text{Bi}_{0.06})_{\Sigma 2.00}$ , calculated on the basis of 15 atoms per formula unit.

TABLE 4. ELECTRON-MICROPROBE DATA ON TÖRNROOSITE GRAINS FROM BUSHVELD (1-3)\* AND MIESSIJOKI (4-10)

sample	1 AS6444	2 AS6467	3 AS6467	4 400	5 401	6 402	7 403	8 404	9 406	10 408
Pd wt%	74.29	72.84	72.84	72.37	71.62	72.70	72.40	71.89	71.99	72.79
Pt	0.00	0.15	0.22	1.88	1.64	1.73	1.61	1.82	1.68	1.90
Fe	0.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Cu	0.00	0.26	0.00	0.00	0.02	0.00	0.01	0.00	0.00	0.00
S	0.16	0.00	0.23	0.01	0.00	0.02	0.00	0.01	0.00	0.02
As	7.34	9.58	7.15	8.81	8.84	8.68	8.84	8.72	8.89	8.82
Se	0.22	0.00	0.26	0.10	0.01	0.04	0.00	0.11	0.04	0.07
Sn	0.36	0.33	0.95	2.16	2.16	2.15	2.09	2.13	2.09	2.08
Sb	1.11	5.33	0.88	0.81	0.89	0.82	0.89	0.81	0.85	0.83
Te	16.24	9.50	15.70	12.87	13.20	13.34	13.13	13.20	13.56	13.34
Bi	0.46	0.78	0.37	0.74	0.78	0.70	0.81	0.84	0.89	0.75
Total	100.26	98.76	98.61	99.75	99.16	100.18	99.78	99.53	99.99	100.61
Pd at.%	73.71	72.66	73.47	72.49	72.17	72.54	72.50	72.25	72.01	72.33
Pt	0.00	0.08	0.12	1.03	0.90	0.94	0.88	1.00	0.92	1.03
Fe	0.17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02
Cu	0.00	0.44	0.00	0.00	0.03	0.00	0.02	0.00	0.00	0.00
S	0.54	0.00	0.78	0.03	0.00	0.07	0.00	0.03	0.00	0.07
As	10.34	13.58	10.24	12.53	12.65	12.30	12.57	12.45	12.63	12.45
Se	0.29	0.00	0.35	0.14	0.01	0.05	0.00	0.15	0.05	0.09
Sn	0.32	0.29	0.86	1.94	1.95	1.92	1.88	1.92	1.87	1.85
Sb	0.97	4.64	0.78	0.71	0.78	0.72	0.78	0.71	0.74	0.72
Te	13.43	7.90	13.21	10.75	11.09	11.10	10.97	11.06	11.31	11.06
Bi	0.23	0.39	0.19	0.38	0.40	0.36	0.41	0.43	0.45	0.38
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Pd apfu	11.06	10.90	11.02	10.87	10.83	10.88	10.87	10.84	10.80	10.85
Pt	0.00	0.01	0.02	0.15	0.14	0.14	0.13	0.15	0.14	0.15
Fe	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cu	0.00	0.07	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
S	0.08	0.00	0.12	0.00	0.00	0.01	0.00	0.01	0.00	0.01
As	1.55	2.04	1.54	1.88	1.90	1.85	1.89	1.87	1.89	1.87
Se	0.04	0.00	0.05	0.02	0.00	0.01	0.00	0.02	0.01	0.01
Sn	0.05	0.04	0.13	0.29	0.29	0.29	0.28	0.29	0.28	0.28
Sb	0.14	0.70	0.12	0.11	0.12	0.11	0.12	0.11	0.11	0.11
Te	2.02	1.19	1.98	1.61	1.66	1.67	1.64	1.66	1.70	1.66
Bi	0.03	0.06	0.03	0.06	0.06	0.05	0.06	0.06	0.07	0.06

\* Oberthür *et al.* (2004). The formulae are recalculated on the basis of 15 atoms per formula unit.

of 10 electron-microprobe analyses and 15 atoms per formula unit, is  $(\text{Pd}_{10.85}\text{Pt}_{0.14})_{\Sigma 10.99}(\text{As}_{1.88}\text{Sb}_{0.11})_{\Sigma 1.99}(\text{Te}_{1.65}\text{Sn}_{0.29}\text{Bi}_{0.06})_{\Sigma 2.00}$ . The physical properties of törnroosite, isomertieite are slightly different: the reflectance values (Fig. 3, Table 1) are highest in isomertieite, lowest in törnroosite and intermediate in müssiite, whose reflectance curve crosses those of isomertieite and törnroosite. The VHN hardness (Table 6) is highest in isomertieite and lowest in müssiite, with the VHN of törnroosite being quite close to that of isomertieite. The differences in reflectance values and hardness may be due to differences in density, hardness and atomic number, given the presumed substitution of As, Sb, Se, Te and Bi. Figure 4A shows the linear correlation that exists between As and Sb + Sn + Te + Bi of isomertieite, törnroosite and mertieite II, respectively. Figure 4B documents the relationship of törnroosite to

other relevant phases in the system (Pt + Pd) – As – (Sb + Sn + Te + Bi). Törnroosite represents the second mineral directly related to isomertieite, and they actually represent a group having the same structure with anions substituting each other in the lattice. Thus, the negative slope shown in Figure 4A, indicative of Sb + Te + Sn + Bi  $\leftrightarrow$  As substitution, is to be expected.

Previously, minerals with chemical compositions similar to those of törnroosite have been reported by Oberthür *et al.* (2004) and Grokhovskaya *et al.* (2009). The PGE placer minerals described in the study of Oberthür *et al.* (2004) were collected from the Maandagshoek farm, Eastern Bushveld, from sediments of the Moopetsi River, which crosses both the UG-2 and Merensky Reef, and which is close to the platiniferous dunite pipes of Driekop, Mooihoek and Onverwacht. In this study, the chemical compositions of phases similar

TABLE 5. COMPARATIVE DATA FOR TÖRNROOSITE AND RELATED MINERALS

	törnroosite	isomertieite <sup>1</sup>	miessiite <sup>2</sup>
Formula	Pd <sub>11</sub> As <sub>2</sub> Te <sub>2</sub>	Pd <sub>11</sub> As <sub>2</sub> Sb <sub>2</sub>	Pd <sub>11</sub> Se <sub>2</sub> Te <sub>2</sub>
Crystal system	Cubic	Cubic	Cubic
Space group	Fd $\bar{3}$ m	Fd $\bar{3}$ m	Fd $\bar{3}$ m
a (Å)	12.3530(4)	12.283(2)	12.448(2)
V (Å <sup>3</sup> )	1885.03(1)	1853.16(1)	1929.0(4)
Z	8	8	8
Strongest XRD lines (l, d) hkl	(11, 2.519) 422 (90, 2.376) 511, 333 (100, 2.182) 440 (13, 1.862) 622 (11, 1.608) 731, 553 (14, 1.544) 800 (13, 1.2606) 844 (11, 0.8253) <u>1284</u>	(90, 2.356) 511 (100, 2.167) 440 (70, 1.533) 800 (60, 1.446) 660 (60, 1.287) 931 (70, 1.253) 844 (60, 1.234) 933 (70, 1.188) 951	(80, 2.395) 511, 333 (100, 2.197) 440 (25, 1.875) 622 (25, 1.555) 800 (25, 1.305) 931 (30, 1.271) 844

<sup>1</sup> Clarke *et al.* (1974), <sup>2</sup> Kojonen *et al.* (2007).

TABLE 6. COMPARATIVE DATA ON HARDNESS FOR TÖRNROOSITE, ISOMERTIEITE AND MIESSIITE

	törnroosite	isomertieite	miessiite
VHN <sub>avg</sub> range	519 509–536	592 587–598	362 348–370
Mohs hardness	5	5.5	2–2½

Data for isomertieite from Cabri (2002), and for miessiite, from Kojonen *et al.* (2007).

to törnroosite were compared with those published by Törnroos *et al.* (1996), leading to the conclusion that they could be the same mineral. This mineral occurs intergrown with vasilite, Pt–Fe alloy, laurite, stillwaterite, and has oriented exsolution-type inclusions of keithconnite. Interestingly, a very small grain ( $\sim 10 \times 5 \mu\text{m}$ ) of a phase corresponding to Pd<sub>11</sub>Sb<sub>2</sub>Te<sub>2</sub> was discovered intergrown with Pt–Fe alloy, Pt–Fe–Cu alloy, native Ru–Ir–Os–Pt alloy and rhodarsenide (Rh,Pd)<sub>2</sub>As (F. Melcher, pers. commun. 2010). The distribution of different PGM phases in the placer from the Moopetsi River does not correspond to the PGM in the Merensky Reef or in UG–2, but might also reflect contributions of PGM from the Mooihoek, Onverwacht and Driekop pipes, with abundant Pt–Fe alloys. For example, the PGM found in the Merensky Reef are typically 10–200  $\mu\text{m}$  in size, whereas those from the UG–2 are much smaller, commonly  $< 10$ –30  $\mu\text{m}$ . In the Driekop pipe, Pt–Fe alloy grains make up 50 vol.% of the PGM, sperrylite and geversite 30 vol.%, hollingworthite–iarasite 15 vol.%, and the remaining 5 vol.% consists of stibiopalladinite, cooperite, laurite, stumpflite, braggite, native Os, Ir–Os, Os–Ir, and unnamed minerals (Pt,Pd) (Bi,Sb) and (Pt,Pd)<sub>3</sub>Sb<sub>2</sub> (Tarkian & Stumpf 1975). It

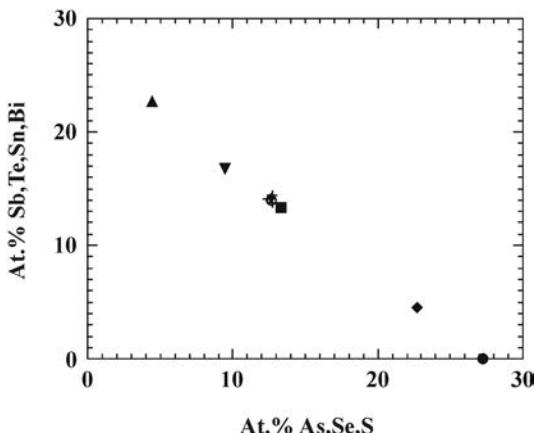


Fig. 4A. Compositions of the Bushveld and Miessijoki törnroosites plotted in an XY diagram. The symbols are defined in Figure 4B.

is notable that Pt–Fe alloy can occur in crystals up to 1 mm in size. Cabri *et al.* (1977a, 1977b) described Pt–Fe alloy, various Pt–Fe–Cu–Ni alloys, platarsite, genkinite, sperrylite, stibiopalladinite, rutharsenite, and mertieite II from the Onverwacht pipe. From the Mooihoek and Onverwacht pipes, Rudashevsky *et al.* (1992) have reported about 15 PGM, including Pt–Fe alloy, sperrylite, hollingworthite, platarsite and laurite in grains up to 100  $\mu\text{m}$  in size. Notably, whereas PGE sulfides are largely absent from these pipes (except for rare hollingworthite and laurite), they are abundant in the Merensky Reef and UG–2. Additional PGM in the reefs include bismuthotellurides, sulfarsenides and rare PGM of Pt, Pd, As, Sb and Te compositions.

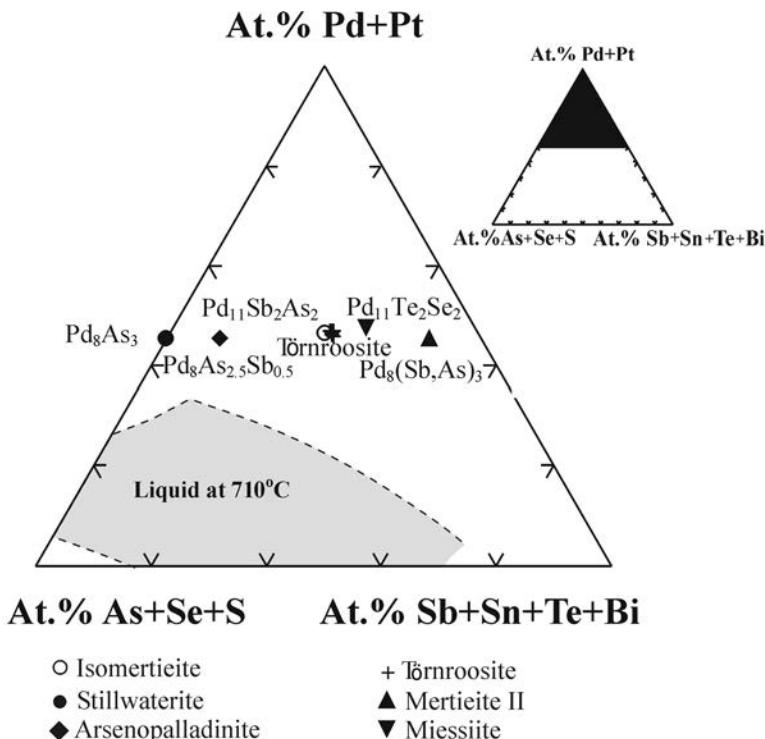


FIG. 4B. Compositions of the Bushveld and Miessijoki törnroosite plotted in terms of Pd + Pt – As + Se + S – Sb + Sn + Te + Bi. The experimental results shown pertain to the system Pd–As–Sb (Cabri *et al.* 1975).

Grokhovskaja *et al.* (2009) studied the PGE mineralogy of the Monchétundra deposit, Kola Peninsula, Russia, and discovered *ca.* 50 PGE-bearing minerals, metal alloys, oxides and hydroxides. Among the 18 unknown PGE-bearing minerals reported, the authors included Pd<sub>11</sub>As<sub>2</sub>Te<sub>2</sub> from the South Sopcha pluton. Unfortunately, no analytical data for this phase were provided. The PGM observed include primary magmatic Pt–Fe alloys, tulameenite, skaergaardite, nielsenite, Au–Ag alloys and secondary alloys consisting of Pt, Pd, Ni, Cu, Fe. The sulfides present are laurite, cooperite or braggite, and vysotskite. The arsenides are sperrylite, guanglinite, palladoarsenide, vincentite, menshikovite, irarsite, hollingworthite and platarsite. Antimonides and tellurides include isomertieite, mertieite II, stibiopalladinite, kotulskite, moncheite, michenerite, merenskyite, telluropalladinite, keithconnite, telargpalite, sopherite, and hessite. Zvyagintsevite, Pd<sub>3</sub>Pb, also was reported. Grokhovskaja *et al.* (2009) interpreted the Monchétundra PGE deposit to be a magmatic layered intrusion that has been strongly tectonized and hydrothermally altered, as both primary magmatic and secondary PGE minerals are present.

Experimental results of the ternary system Pd–As–Te are not known, but comparing the diagram in Figure 4B with the experimental results of Cabri *et al.* (1975) in the ternary system Pd–As–Sb, it is evident that the composition törnroosite plots in the field of solid phases near isomertieite composition at a temperature of 710°C. The unidentified phase of composition Pd<sub>11</sub>Sb<sub>2</sub>Te<sub>2</sub> reported by Oberthür *et al.* (2004) from the eastern part of the Bushveld complex may also be isostructural with törnroosite (F. Melcher, pers. commun., 2010), stable below 800°C in the system Pd–Sb–Te–As, along with the minerals isomertieite and törnroosite. Barkov *et al.* (2008) described Te-bearing isomertieite with an empirical formula (Pd<sub>10.96</sub>Fe<sub>0.03</sub>)<sub>Σ10.99</sub>(Sb<sub>1.13</sub>Te<sub>0.94</sub>)<sub>Σ2.07</sub>As<sub>1.93</sub> as an inclusion in Pt–Fe alloy from the PGM placers of British Columbia, Canada. This phase is chemically intermediate between isomertieite and törnroosite and could represent an example of a mineral with a disordered isomertieite structure.

The occurrence of Pt–Fe and Os–Ir–Ru alloys in the coarse-grained placers of the Miessijoki River suggests that the source of these placers is still not known but

could be similar to the dunite pipes of South Africa. The abundance of relatively soft isomertieite-group minerals, along with Pt-Pd sulfides, selenides, bismuthotellurides and tellurides, suggest that these PGM have not been transported over large distances in the glacio-fluvial processes. Thus, the source for observed PGM is likely to be found in ultramafic intrusions within a few kilometers distance.

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#### REFERENCES

- BARKOV, A.Y., MARTIN, R.F., FLEET, M.E., NIXON, G.T. & LEVISON, V.M. (2008): New data on associations of platinum-group minerals in placer deposits of British Columbia, Canada. *Mineral. Petrol.* **92**, 9-29.
- CABRI, L.J. (2002): The platinum-group minerals. In *The Geology, Geochemistry, Mineralogy and Mineral Beneficiation of Platinum-Group Elements* (L.J. Cabri, ed.). *Can. Inst. Mining Metallurgy, Spec. Vol.* **54**, 13-129.
- CABRI, L.J., LAFLAMME, J.H.G. & STEWART, J.M. (1977b): Platinum-group minerals from Onverwacht. II. Platarsite, a new sulfarsenide of platinum. *Can. Mineral.* **15**, 385-388.
- CABRI, L.J., LAFLAMME, J.H.G., STEWART, J.M., ROWLAND, J.F. & CHEN, T.T. (1975): New data on some palladium arsenides and antimonides. *Can. Mineral.* **13**, 321-335.
- CABRI, L.J., ROSENZWEIG, A. & PINCH, W.W. (1977a): Platinum-group minerals from Onverwacht. I. Pt-Fe-Cu-Ni alloys. *Can. Mineral.* **15**, 380-384.
- CLARKE, A.M., CRIDDLE, A.J. & FEJER, E.E. (1974): Palladium arsenide-antimonides from Itabira, Minas Gerais, Brazil. *Mineral. Mag.* **39**, 528-543.
- CRIDDLE, A.J. & STANLEY, C.J., eds. (1993): *Quantitative Data File for Ore Minerals* (3<sup>rd</sup> edition). Chapman & Hall, London, U.K.
- GROKHOVSKAJA, T.L., LAPINA, M.I. & MOKHOV, A.V. (2009): Assemblages and genesis of platinum-group minerals in low-sulfide ores of the Mochetundra deposit, Kola Peninsula, Russia. *Geology of Ore Deposits* **51**, 467-485.
- KOJONEN, K., OJALA, V.J., TARKIAN, M. & TÖRNROOS, R. (2006a): New observations of the Au and PGE nuggets in the Ivalojoki and Lemmenjoki areas, Finnish Lapland. *Nordic Geological Winter Meeting (Oulu), Abstr. Vol.*
- KOJONEN, K., TARKIAN, M., KNAUF, V.V., TÖRNROOS, R. & HEIDRICH, S. (2006b): Placer platinum-group minerals from Ivalojoki and Lemmenjoki rivers, Finnish Lapland. *Int. Mineral. Assoc., 19<sup>th</sup> Gen. Meeting (Kobe), Program Abstr.*, 196.
- KOJONEN, K.K., TARKIAN, M., ROBERTS, A.C., TÖRNROOS, R. & HEIDRICH, S. (2007): Miessite,  $Pd_{11}Te_2Se_2$ , a new mineral species from Miessijoki, Finnish Lapland, Finland. *Can. Mineral.* **45**, 1221-1227.
- MCDONALD, A.M. & CABRI, L.J. (2005): Problems and solutions in the mertieite clan of platinum-group minerals: the important role of single-crystal X-ray diffraction analyses in PGM studies. *Geol. Assoc. Can. – Mineral. Assoc. Can., Program Abstr.* **30**, 127.
- MERILÄINEN, K. (1976): The granulite complex and adjacent rocks in Lapland, northern Finland. *Geol. Surv. Finland, Bull.* **281**.
- OBERTHÜR, T., MELCHER, F., GAST, L., WÖHRL, C. & LODZIAK, J. (2004): Detrital platinum-group minerals in rivers draining the Eastern Bushveld complex, South Africa. *Can. Mineral.* **42**, 563-582.
- PANALYTICAL (2006): HIGHSCORE PLUS Software (version 2.2.0). PANalytical B.V., Almelo, The Netherlands.
- PETRUS, J.A., ROSS, K.C. & MCDONALD, A.M. (2011): DIIS: a cross-platform program for the reduction of X-ray diffraction data from a cylindrical area detector. *Comput. Geosci.* (in press).
- RUDASHEVSKY, N.S., AVDONTESEV, S.N. & DNEPROVSKAYA, M.B. (1992): Evolution of PGE mineralization in hornblonitic dunites of the Mooihoek and Onverwacht pipes, Bushveld Complex. *Mineral. Petrol.* **47**, 37-54.
- STRUNZ, H. & NICKEL, E.H. (2001): *Strunz Mineralogical Tables* (9<sup>th</sup> ed.). E. Schweizerbart'sche Verlagsbuchhandlung (Nägele u. Obermiller), Stuttgart, Germany.
- TARKIAN, M. & STUMPFL, E.F. (1975): Platinum mineralogy at the Driekop mine, South Africa. *Mineral. Deposita* **10**, 71-75.
- TUISKU, P. & HUHMA, H. (2003): Provenance of the Lapland Granulite Belt: evidence for silicic crustal accretion at 2.1–1.97 Ga. *Geophysical Research Abstr.* **5**, 12121.
- TÖRNROOS, R., JOHANSON, B. & KOJONEN, K. (1996): Alluvial nuggets of platinum-group minerals and alloys from Finnish Lapland. *Int. Geol. Correlation Program, Project 336 Symposium (Rovaniemi), Program Abstr.*, 85-86.

