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Pd–Ag TELLURIDES FROM A Cl-RICH ENVIRONMENT IN THE LUKKULAISVAARA LAYERED INTRUSION, NORTHERN RUSSIAN KARELIA

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ABSTRACT

Rare Pd–Ag tellurides, telargpalite and the phase Pd_6AgTe_4 occur in pods <0.5 m across and stringers of altered coarse-grained gabbronorite enriched in base-metal sulfides (up to ~25 vol.%) in the Nadezhda deposit, located in a sill-like body of microgabbronorite within the layered series of the Lukkulaisvaara intrusion, Karelia, Russia. The magmatic texture and relics of igneous minerals are preserved in the pods. The associated minerals are various platinum-group minerals (*PGM*), a rare Re-rich sulfide, and highly aluminous secondary minerals, *e.g.*, almandine, Cl-rich ferropargasite, microcrystalline staurolite, and corundum, which formed at the expense of primary plagioclase and enstatite at a deuteric stage. Micro-inclusions of Cl-rich amphibole are common in various *PGM* and associated chalcopyrite at Nadezhda. The telargpalite displays an atomic ratio (Pd + Ag):(Te + Bi + Pb) of 3. The Ag–Pd correlation is negative and strong, and implies a limited Ag-for-Pd substitution in telargpalite, the empirical formula being $Pd_{2-x}Ag_{1+x}(Te,Bi,Pb)$, where $0 < x < 0.3$. A limited Pd-for-Ag substitution appears to occur in the unnamed Pd_6AgTe_4. The maximum reflectance of the Pd–Ag tellurides increases with an increase in their Pd:Ag ratio. The telargpalite may cut almandine, and thus seems to have formed at a temperature lower than the temperature of equilibration of garnet–hornblende and garnet–staurolite (~560 to 670°C). The unnamed Pd_6AgTe_4 occurs in a close association with a Cl-dominant analogue of ferropargasite (up to 4.5 wt.% Cl; 1.2 Cl atoms per formula unit). The pods and stringers rich in Pd, Pt and Ag probably formed by crystallization of isolated volumes of H_2O-saturated melt, *in situ*. The Pd–Ag tellurides formed in a volatile-rich deuteric environment, at relatively low temperatures, and Cl was prominent in the fluid causing the alteration.

Keywords: platinum-group minerals, Pd–Ag tellurides, telargpalite, Pd_6AgTe_4, Cl-rich amphibole, layered intrusion, Lukkulaisvaara, Karelia, Russia, Fennoscandian Shield.

SOMMAIRE

De rares tellurures de Pd–Ag, y compris la telargpalite et une phase méconnue, Pd_6AgTe_4, ont été mis en évidence dans des lentilles de moins de 0.5 m de taille et des veines de gabbronorite à gros grains altérée et enrichie en sulfures de métaux de base (jusqu'à environ 25% par volume) dans le gisement de Nadezhda, situé dans un massif de microgabbronorite en filon-couche de la série stratifiée du complexe intrusif de Lukkulaisvaara, en Karélie, Russie. La texture magmatique et les reliques des minéraux ignés sont préservées dans ces lentilles. Y sont associés des minéraux du groupe du platine, un rare sulfure enrichi en rhénium, et des minéraux secondaires fortement alumineux, par exemple almandin, ferropargasite riche en chlore, staurolite microcristalline, et corindon, qui se seraient formés aux dépens du plagioclase et de l'enstatite primaires. Des micro-inclusions de ferropargasite riche en chlore sont répandues dans divers minéraux du groupe du platine et dans la chalcopyrite associée à Nadezhda. La telargpalite possède un rapport atomique (Pd + Ag):(Te + Bi + Pb) de 3. La corrélation Ag–Pd est négative et excellente, ce qui implique une subtitution de Ag pour Pd limitée dans la telargpalite, la formule empirique étant $Pd_{2-x}Ag_{1+x}(Te,Bi,Pb)$, $0 < x < 0.3$.

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Une substitution limitée de Pd pour Ag affecte le minéral sans nom, Pd_6AgTe_4. La réflectance maximale des tellurures de Pd–Ag augmente avec une augmentation du rapport Pd:Ag. La telargpalite semble recouper l'almandin, et pourrait ainsi avoir cristallisé à une température inférieure à l'équilibre grenat–hornblende et grenat–staurolite (~560 à 670°C). Le minéral sans nom montre une association étroite avec l'analogue à dominance de chlore de la ferropargasite (jusqu'à 4.5% Cl en poids; 1.2 atomes de Cl par unité formulaire). Les lentilles et les veines riches en Pd, Pt et Ag auraient cristallisé à partir de volumes isolés de magma saturé en H_2O, *in situ*. Les tellurures de Pd–Ag se sont formés dans un milieu deutérique riche en phase volatile, à une température relativement faible. Le chlore semble avoir été important dans la phase fluide responsable de l'altération.

(Traduit par la Rédaction)

Mots-clés: minéraux du groupe du platine, tellurures de Pd–Ag, telargpalite, Pd_6AgTe_4, amphibole riche en Cl, complexe igné stratiforme, Lukkulaisvaara, Karélie, Russie, bouclier fennoscandien.

INTRODUCTION

The two known platinum-group minerals (*PGM*) and unnamed phases in the system Pd–Ag–Te are rare. Telargpalite [$(Pd,Ag)_3(Te,Bi,Pb)$] was first discovered in the Noril'sk complex of Siberia, Russia (Kovalenker *et al*. 1974), and was subsequently reported from the Lukkulaisvaara layered intrusion, in Russian Karelia (Begizov & Batashev 1981, Barkov & Lednev 1993). A micrometric grain of telargpalite has been documented in a fluid inclusion in a sulfide mineral from the Coldwell complex (Watkinson & Jones 1996). Sopcheite ($Ag_4Pd_3Te_4$) was first described from Sudbury, Ontario, as unnamed $Ag_4Pd_3Te_4$ (Cabri & Laflamme 1976), and was named after the Sopcha Pd–Pt deposit in the Monchegorsk layered complex, Kola Peninsula, Russia (Orsoev *et al.* 1982). Since then, a number of occurrences of sopcheite have been reported from Canada (Dunning *et al*. 1984, Mulja & Mitchell 1990) and from Russia (Trofimov *et al.* 1990, Barkov & Lednev 1993).

In this paper, we focus on the occurrence, association, and characteristics of Pd–Ag tellurides (telargpalite and unnamed Pd_6AgTe_4), which are associated with an unusual Cl–(Al)-rich assemblage of secondary minerals from the Nadezhda platinum-group element (*PGE*) deposit, Lukkulaisvaara intrusion, Oulanka (or Olanga) layered complex, northern Karelia, Russia.

OCCURRENCE

The Lukkalaisvaara layered intrusion is Early Proterozoic in age (2437 ± 11 Ma: U–Pb dating of zircon and baddeleyite: Barkov 1992). The intrusion is predominantly composed of various gabbronorites and subordinate olivine-rich cumulates, which occur at a lower stratigraphic level (Fig. 1). Major zones of *PGE* mineralization, present in this intrusion, are associated with bodies of microgabbronorite hosted by mafic rocks of the layered series (*e.g.*, Begizov & Batashev 1981, Grokhovskaya *et al*. 1992, Barkov *et al*. 1995a, b, Barkov *et al.* 1996, Glebovitsky *et al*. 2001).

In the Nadezhda *PGE* deposit (Fig. 1), telargpalite and the unnamed Pd_6AgTe_4 occur in pods and stringers (<0.5 m across) of coarse-grained to pegmatitic gabbronorite gradational into plagioclase-bearing pyroxenite that are located within a sill-like body of microgabbronorite, close to its center. The sill-like body, ≤0.2 km thick, is located within a gabbronorite sequence of the layered series.

Compared with the surrounding mafic rocks of the layered series, the microgabbronorite is characterized by low concentrations of incompatible elements (Zr, Ti, *etc.*) and relatively high values of normative diopside (Barkov 1992). On the basis of these distinctions and field observations, this sill-like body of microgabbronorite was considered to represent a batch of new magma (Barkov 1992).

TABLE 1. PRIMARY AND SECONDARY MINERALS IN PGE-RICH ALTERED COARSE-GRAINED GABBRONORITE FROM THE LUKKULAISVAARA LAYERED INTRUSION

Mineral	P	S	Details[§]
Enstatite	▣		$Wo_{3.7–4.6}En_{74.7–76.5}Fs_{19.3–21.4}$ (~50 to 70 vol.%)
Plagioclase	▣		An_{61} to An_{59} (~10 to 40 vol.%)
Augite	▣		$Wo_{41.1–43.4}En_{43.9–49.0}Fs_{9.4–12.7}$ (<10 vol.%)
Magnetite	▣		Up to ~10 vol.%
Ferropargasite (Cl-rich)		▣	Matrix minerals, veins and rims the primary plagioclase, minute subhedral to euhedral inclusions in chalcopyrite, oulankaite and other platinum-group minerals, and inclusions in staurolite
Almandine		▣	Product of replacement of primary plagioclase (grains up to ~4 mm)
Staurolite		▣	Formed at the expense of primary plagioclase and enstatite. Subhedral crystals (<0.3 mm) and intergrowths with Al-rich amphiboles and almandine
Epidote		▣	Product of replacement of primary plagioclase
Chlorite		▣	Product of replacement of primary plagioclase
Hercynite (Zn-rich)		▣	Anhedral grains (<0.2 mm)
Phlogopite (Cl-rich)		▣	Small (<40 μm) inclusions in chalcopyrite
Corundum		▣	Anhedral grains (≤0.1 mm)
Al_2SiO_5		▣	Anhedral grains (≤50 μm)
AlO(OH)		▣	Rim around corundum
Actinolite		▣	Product of replacement of primary enstatite
Tremolite		▣	Product of replacement of primary enstatite
Cummingtonite or anthophyllite		▣	Product of replacement of primary enstatite
Talc		▣	Pseudomorph after enstatite
Quartz		▣	Grains and veinlets (≤0.2–0.3 mm).

[§] Barkov *et al.* (1999). P: primary, S: secondary (alteration-induced).

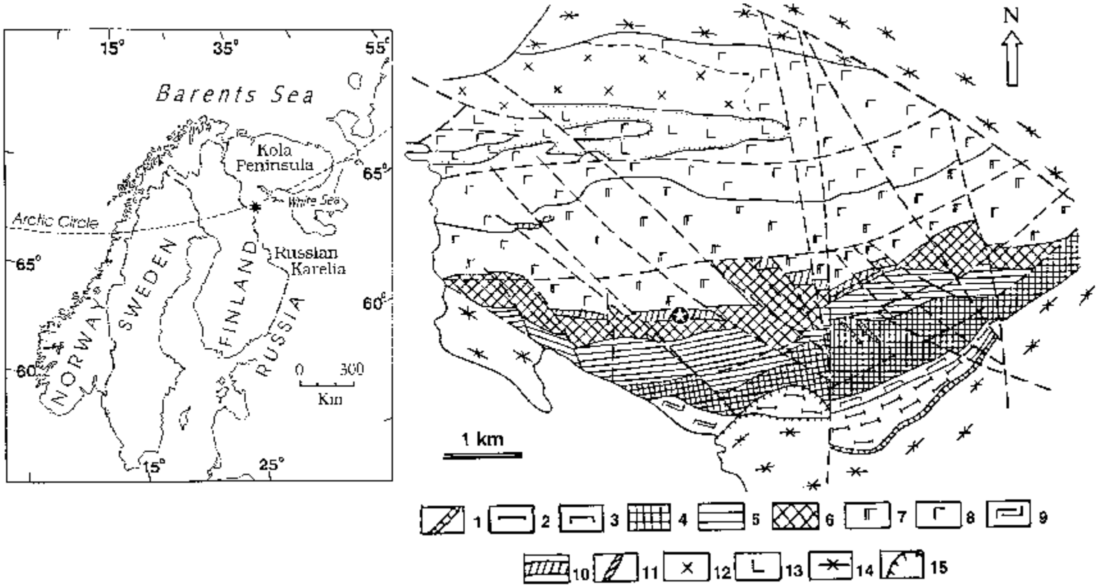


FIG. 1. Geological map of the Lukkulaisvaara layered intrusion (Klyunin *et al.*, unpublished map; reproduced from Grokhovskaya *et al.* 1992); location of the intrusion in the Fennoscandian Shield is shown by a filled star in the inset. 1: gabbronorite of the Marginal zone, 2: Peridotite zone, 3: Pyroxenite zone, 4: Lower Norite zone, 5: Critical zone, 6: Upper Norite zone, 7: Gabbronorite zone, 8: Gabbro zone, 9: coarse-grained gabbro, 10: microgabbronorite, 11: diabase dikes, 12: diorite plagioclase porphyry and granophyric granite, 13: volcanic rocks, 14: diorite gneiss and plagiogranite, 15: faults. Location of the occurrence of Pd–Ag tellurides, the Nadezhda *PGE* deposit, is shown by an open star.

Typically, the pods and stringers display a sharp contact with the host microgabbronorite, which is relatively fresh (Fig. 2). Primary rock-forming silicates of the telluride-bearing pods display the same range of composition as in the host microgabbronorite (Table 1), which implies a close genetic relationship and an apparent equilibrium between the pods and their host rock (Barkov *et al.* 1999).

The pods and stringers are enriched in the *PGE* and Ag, mostly in Pd, and contain abundant base-metal sulfides (*BMS*), dominantly chalcopyrite, bornite, millerite and subordinate pentlandite (up to ~20–25 vol.%). A member or members of the linnaeite group and sphalerite are accessories; magnetite is abundant in places (up to 10 vol.%). Though the *PGE*-rich coarse-grained rocks may display various extents of alteration, their primary texture and relics of igneous minerals (plagioclase and orthopyroxene) are typically well preserved (Fig. 2). An unusual assemblage of aluminous secondary minerals, including Al–(Cl)-rich amphibole, almandine and microcrystalline staurolite, is present in a *PGE*-rich coarse-grained gabbronorite in association with various *PGM* (Barkov *et al.* 1999).

The *PGE*-rich pods and stringers contain a wide variety of *PGM* (Table 2), including a number of rare species, such as the Pd–Ag tellurides oulankaite [$(Pd,Pt)_5(Cu,Fe,Ag)_4SnTe_2S_2$] (Barkov *et al.* 1996) and its Ag-dominant analogue (Barkov *et al.*, unpubl. data), and an unnamed rhenium-rich sulfide [$(Cu,Fe)(Re,Mo)_4S_8$] (Barkov & Lednev 1993).

TABLE 2. MINERALS OF PRECIOUS METALS IN THE PGE-RICH ALTERED COARSE-GRAINED GABBRONORITE, NADEZHDA PGE DEPOSIT, LUKKULAISVAARA INTRUSION

	Common	Subordinate	Rare
Telargpalite	▣		
Moncheite	▣		
Oulankaite§	▣		
Kotulskite		▣	
Braggite series		▣	
Tulameenite		▣	
Sperrylite			▣
Zvyagintsevite			▣
Atokite rustenburgite			▣
Intermetallic phase*			▣
Ag-rich oulankaite			▣
Irarsite			▣
Telluropalladinite (?)			▣
Unnamed $(Cu,Fe)(Re,Mo)_4S_8$**			▣

§ Barkov *et al.* (1996).
* "Stannopalladinite": $(Pd_{2.30}Cu_{0.46}Pt_{0.21}Fe_{0.02})_{\Sigma 2.99}Sn_{1.01}$ [or $(Pd,Pt)_3CuSn_2$].
** Barkov & Lednev (1993).

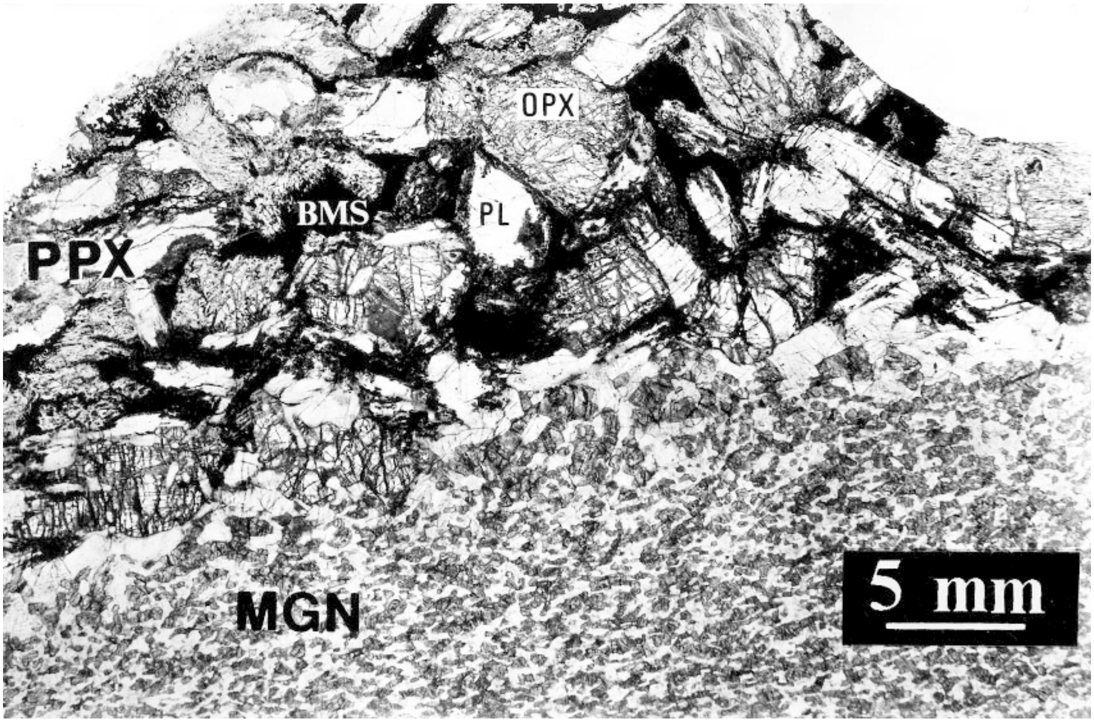


FIG. 2. Photomicrograph showing a contact between the host microgabbronorite (MGN) and a coarse-grained orthopyroxene-*PGE*-rich gabbronorite (grading to plagioclase-bearing pyroxenite), PPX, at Lukkulaisvaara. The primary texture of the coarse-grained rock (mineralized pods and stringers) is well preserved, and the host microgabbronorite is quite fresh. OPX: orthopyroxene, PL: plagioclase, BMS: base-metal sulfides. Thin polished section; parallel nicols.

ANALYTICAL METHODS

Pd–Ag tellurides

Various analytical facilities were used to analyze the Pd–Ag tellurides. A JEOL–8900 electron microprobe was operated at an accelerating voltage of 20 kV and a beam current of 30 nA. The X-ray lines used were Pd*L*α, Ag*L*β, Pt*M*α, Te*L*α, Pb*M*α and Bi*M*α. Pure elements, synthetic $AgBiSe_2$ (for Ag and Bi) and galena were used as standards.

A JEOL–8600 electron microprobe was operated at an accelerating voltage of 25 kV and a beam current of 30 nA (35 nA for Pt and Bi). The X-ray lines used were Pd*L*α, Ag*L*β, Pt*L*α, Te*L*α, and Bi*M*α. The standards were pure elements.

The quantitative energy-dispersion analyses were carried out using a JEOL JSM–6400 scanning-electron microscope equipped with a LINK eXL energy-dispersion spectrometer. Analytical conditions were 15 kV and 1.2 nA. The X-ray lines were Pd*L*, Ag*L*, Te*L* and Bi*M*. The standards were pure elements and $PtTe_2$. Counting periods of 100 seconds were applied. The beam size was about ~1 μm. The spectra were processed by ZAF–4 program and Link ISIS (version 3.00) on-line program.

Cl-rich amphibole

A JEOL-8900 electron microprobe was operated at an accelerating voltage of 20 kV and a beam current of 22 nA (spot size: 1μm). The following standards were used: diopside (Si, Mg, and Ca), synthetic TiO_2 (Ti), orthoclase (K and Al), Fe_2O_3 (Fe), chromite (Cr), albite (Na), spessartine (Mn), NiO (Ni), CaF_2 (F), and vanadinite (Cl).

A JEOL–733 electron microprobe was operated at an accelerating voltage of 15 kV and beam current of 15 nA. The following standards were used: wollastonite (Si, Ca), MgO (Mg), orthoclase (K), jadeite (Na), pure Fe, Mn, and Ni, and Al_2O_3. The amphibole was analyzed for chlorine using tugtupite (SPI Supplies) and KCl as standards.

A JEOL–8600 electron microprobe was operated at an accelerating voltage of 15 kV (20 kV for Ni), and a beam current of 10.5 nA (35.5 nA for Ni). We used as standards augite (Si), forsterite (Mg), orthoclase (K), albite (Na), fayalite (Fe), diopside (Ca), rhodonite (Mn), pure Ni, anorthite (Al), and sodalite (Cl).

THE PALLADIUM–SILVER TELLURIDES

Telargpalite: textural relationships

Though telargpalite is rare in other complexes, it is one of the principal *PGM* in the Nadezhda *PGE* deposit. Typically, telargpalite forms inclusions (up to ~0.2 mm across) in chalcopyrite and occurs in intergrowth with other *PGM*, such as moncheite, kotulskite, oulankaite, argentian oulankaite, and tulameenite. Examples of intergrowths of telargpalite and moncheite are shown in Figure 3. Moncheite is characteristically surrounded and "corroded" by telargpalite in such intergrowths (Figs. 3b, c), and these *PGM* may commonly contain micro-inclusions of hydrous silicates, quite abundant in places (*e.g.*, Fig. 3b). The presence of a thin rim of tulameenite is noteworthy; it is only developed along the telargpalite–chalcopyrite border and is absent where the telargpalite is in contact with silicate minerals (Figs. 3a, b). This rim thus seems to have formed by a subsolidus reaction involving the adjacent chalcopyrite as a source of Cu and Fe present in the tulameenite. Telargpalite is quite commonly associated with hydrous silicates and other secondary minerals, especially with a Cl-rich amphibole (2.1–3.2 wt.% Cl: Figs. 4c, e; see below). Interestingly, telargpalite may cut almandine (Fig. 4f).

Telargpalite: composition and formula

About ten grains of telargpalite from Lukkulaisvaara were analyzed in this study; representative results are presented in Tables 3 to 5. Compared with telargpalite from the Noril'sk complex, the type locality, telargpalite at Lukkulaisvaara is poor in Pb (Table 5).

Two formulae have previously been proposed for telargpalite from Noril'sk: $(Pd,Ag,Bi,Pb)_{4+x}Te$ and $(Pd,Ag)_3(Te,Bi,Pb)$ (Kovalenker *et al.* 1974). The sim-

TABLE 3. SELECTED RESULTS OF ELECTRON-MICROPROBE ANALYSES OF TELARGPALITE FROM THE LUKKULAISVAARA INTRUSION

No.	Pd	Pt	Ag	Te	Bi	Pb	Total
1	42.68	n.d.	30.08	27.50	0.57	n.d.	100.83
2	41.92	n.d.	29.76	24.83	4.33	n.d.	100.84
3	42.28	0.22	30.35	26.88	0.29	0.72	100.74
4	40.98	n.d.	30.70	24.09	3.68	1.19	100.64
5	40.58	n.d.	30.49	23.96	2.59	2.84	100.46
6	40.46	n.d.	30.29	23.52	3.39	2.81	100.47
7	42.81	n.d.	29.15	24.72	3.78	0.26	100.72
8	42.37	n.d.	28.97	25.13	3.92	n.d.	100.39
9	41.75	0.29	28.95	24.20	3.65	1.13	99.97
10	43.01	0.23	29.26	24.67	3.53	n.d.	100.70
11	40.91	0.25	30.01	23.34	3.10	2.62	100.23
12	42.66	0.21	28.67	24.98	3.92	n.d.	100.44
13	43.30	0.28	29.18	27.24	0.65	n.d.	100.65
14	43.38	n.d.	29.48	27.01	0.49	0.24	100.60
15	43.31	n.d.	29.59	27.40	0.21	n.d.	100.51
16	43.41	n.d.	29.38	27.56	n.d.	n.d.	100.35
17	43.49	n.d.	29.10	27.40	n.d.	n.d.	99.99
18	42.91	n.d.	30.17	27.42	n.d.	n.d.	100.50
19	43.01	n.d.	29.55	26.98	0.51	0.23	100.28
20	40.41	n.d.	31.30	23.60	2.75	3.02	101.08
21	43.19	0.23	29.62	27.28	0.24	n.d.	100.56
Mean§	42.73	n.d.	29.82	26.32	1.46	0.46	100.79

The results of wavelength-dispersion analyses (in weight %) were acquired with a JEOL JXA–8900 electron microprobe. n.d.: <0.2 wt.%. As and Se were sought, but not detected.

§ The average result of 41 analyses.

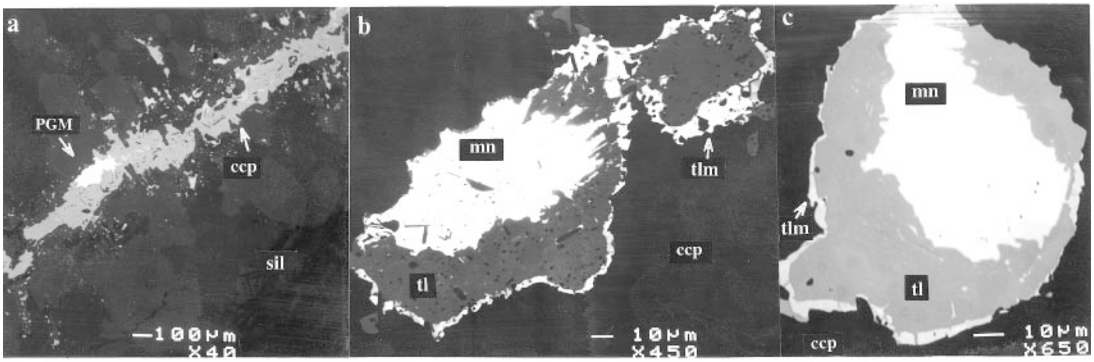
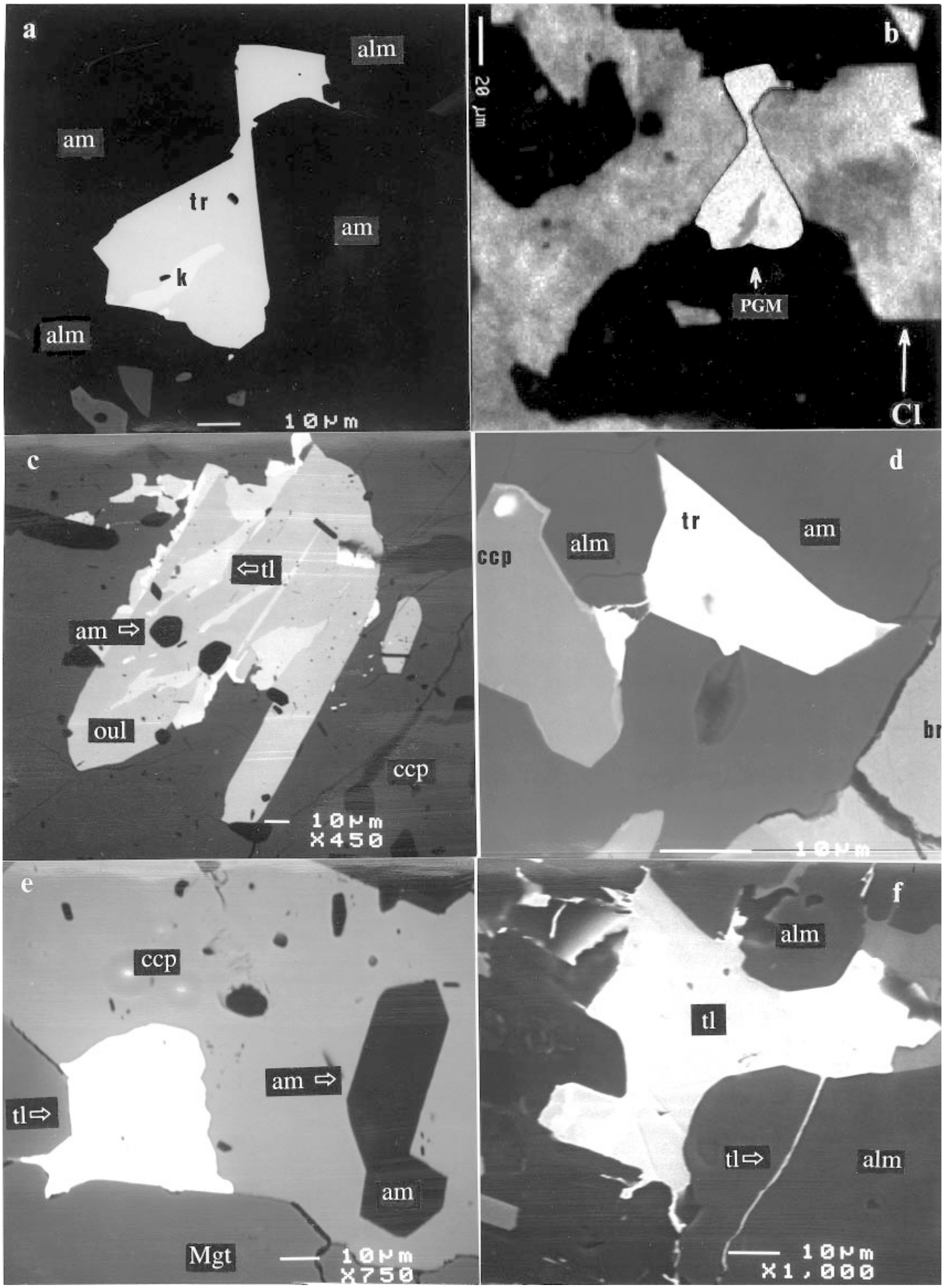


FIG. 3. a. A veinlet of base-metal sulfides (mostly chalcopyrite: ccp), which extends from the coarse-grained gabbronorite to the host microgabbronorite, across their contact shown in Figure 2. Note a large intergrowth of platinum-group minerals (PGM: white) at the boundary of this veinlet. b. Magnification of the grain shown in Figure 3a. Partly resorbed moncheite (mn) is surrounded by telargpalite (tl), and tulameenite (tlm) rims the telargpalite along its contact with the host chalcopyrite (ccp). c. Telargpalite (tl) rims and "corrodes" moncheite (mn). Tlm: a thin rim of tulameenite, ccp: chalcopyrite. Back-scattered electron (BSE) images.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alm
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plified formula $(Pd,Ag)_{4+x}Te$ is commonly cited in the literature; this formula was assumed on the basis of a similarity between X-ray powder patterns of telargpalite and synthetic Pd_4Te of Grønvold & Rost (1956) (Genkin *et al*. 1981).

The atomic ratio (Pd + Ag) : (Te + Bi + Pb) in the compositions of telargpalite from the Lukkulaisvaara intrusion is close to 3 (Tables 3–5), consistent with observations reported from this intrusion (Begizov & Batashev 1981, Barkov & Lednev 1993); they are not consistent with the $(Pd,Ag,Bi,Pb)_{4+x}Te$ and $(Pd,Ag)_{4+x}Te$ formulas. In addition, a substitution relationship involving Pd (Ag) and semimetals is considered highly unlikely; in this respect also, the formula $(Pd,Ag,Bi,Pb)_{4+x}Te$ seems unlikely to be correct.

Though the concentrations of Pd + Ag vary little, a strong negative correlation between Pd and Ag is observed (correlation coefficient $R = –0.97$: Fig. 5), indicating the existence of limited Ag-for-Pd substitution in telargpalite. Thus, Ag likely occupies a separate site in the crystal structure, and the likely formula of telargpalite is $Pd_{2–x}Ag_{1+x}(Te,Bi,Pb)$, where $0 < x < 0.3$.

TABLE 4. COMPOSITION OF TELARGPALITE FROM THE LUKKULAISVAARA INTRUSION, EXPRESSED IN TERMS OF ATOMIC PROPORTIONS*

No.	Pd	Pt	Ag	Σ	Te	Bi	Pb	Σ
1	1.79	-	1.24	3.03	0.96	0.01	-	0.97
2	1.78	-	1.25	3.03	0.88	0.09	-	0.97
3	1.78	<0.01	1.26	3.04	0.94	<0.01	0.02	0.96
4	1.75	-	1.29	3.04	0.86	0.08	0.03	0.97
5	1.74	-	1.29	3.03	0.86	0.06	0.06	0.98
6	1.74	-	1.28	3.02	0.84	0.07	0.06	0.97
7	1.82	-	1.22	3.04	0.88	0.08	<0.01	0.96
8	1.80	-	1.22	3.02	0.89	0.09	-	0.97
9	1.79	<0.01	1.23	3.02	0.87	0.08	0.02	0.97
10	1.82	<0.01	1.22	3.04	0.87	0.08	-	0.95
11	1.76	<0.01	1.27	3.03	0.84	0.07	0.06	0.97
12	1.82	<0.01	1.21	3.03	0.89	0.09	-	0.98
13	1.82	<0.01	1.21	3.03	0.95	0.01	-	0.96
14	1.82	-	1.22	3.04	0.94	0.01	<0.01	0.95
15	1.81	-	1.22	3.03	0.96	<0.01	-	0.96
16	1.82	-	1.22	3.04	0.96	-	-	0.96
17	1.83	-	1.21	3.04	0.96	-	-	0.96
18	1.80	-	1.25	3.05	0.96	-	-	0.96
19	1.81	-	1.23	3.04	0.95	0.01	<0.01	0.96
20	1.72	-	1.31	3.03	0.84	0.06	0.07	0.97
21	1.81	<0.01	1.23	3.04	0.95	<0.01	-	0.95
Mean§	1.80	-	1.24	3.04	0.92	0.03	0.01	0.96

The analytical data are listed in Table 3. § The average result of 41 analyses.
* The atomic proportions are based on four atoms per formula unit.

Unnamed Pd_6AgTe_4: textural relationships

The unnamed Pd_6AgTe_4 is a rare *PGM* in the stringers and pods of coarse-grained altered gabbronorite rich in the *PGE* and Ag (Table 2). This telluride occurs in the rocks enriched in *BMS*. The Pd–Ag telluride is associated with kotulskite, telargpalite and other *PGM*, and typically occurs in small anhedral grains (≤0.1 mm) enclosed within chalcopyrite (commonly near its border with silicate minerals). The Pd–Ag telluride may exhibit vague crystal outlines, which are not well developed, however (Fig. 4a). This telluride also occurs as minute grains (<10 μm) that form part of a polymineralic intergrowth of telargpalite, moncheite, oulankaite, and tulameenite.

The close association of the unnamed Pd_6AgTe_4 with unusually Cl-rich amphibole (up to 4.5 wt.% Cl; see below) is particularly noteworthy (Figs. 4a, d).

Optical properties and microhardness of the Pd–Ag tellurides

In reflected light, the phase Pd_6AgTe_4 is distinctly bireflectant and pleochroic from light gray with a

TABLE 5. RESULTS OF QUANTITATIVE ENERGY-DISPERSION ANALYSES OF TELARGPALITE FROM THE LUKKULAISVAARA INTRUSION

	Weight %						Atomic proportions, *apfu*				
No.	*1*	*2*	*3*	*4*	*5*§	Σ	*1*	*2*	*3*	*4*	*5*§
Pd	40.92	41.47	40.80	41.45	39.1	Pd	1.76	1.78	1.77	1.78	1.72
Ag	29.47	28.89	28.71	28.54	30.0	Ag	1.25	1.22	1.23	1.21	1.31
Te	23.77	24.13	22.88	24.30	20.15	Σ*Me*	3.01	3.00	3.00	2.99	3.03
Bi	5.71	5.95	7.35	6.52	4.0						
Pb	n.d.	n.d.	n.d.	n.d.	6.15	Te	0.86	0.86	0.83	0.87	0.74
						Bi	0.13	0.13	0.16	0.14	0.09
Sum	99.87	100.44	99.74	100.81	99.40	Pb	-	-	-	-	0.14
						Σ	0.99	0.99	0.99	1.01	0.97

§ Telargpalite from Noril'sk (average of two representative compositions from Genkin *et al.* 1981). n.d.: not detected. * The atomic proportions are based on four atoms per formula unit (*apfu*).

FIG. 4. Textural relationships of Pd–Ag tellurides at Lukkulaisvaara. a. Unnamed Pd–Ag telluride, tr (Pd_6AgTe_4), contains an inclusion of kotulskite (k) and occurs at the contact between the Cl-rich ferropargasite (am: up to 4.5 wt.% Cl) and almandine (alm). BSE image. b. X-ray map for chlorine (Cl), combined with a complementary map for Pd, showing a close association between the Pd-rich tellurides, PGM (shown in Fig. 4a) and the Cl-rich amphibole. The vertical scale bar is 20 μm. c. Micro-inclusions of Cl-rich ferropargasite (am: up to 3.3 wt.% Cl) in argentian oulankaite (oul) and telargpalite (tl). ccp: host chalcopyrite. BSE image. d. Unnamed Pd_6AgTe_4 (tr) replacing chalcopyrite (ccp) at the contact of the Cl-rich ferropargasite (am: up to 4.5 wt.% Cl) and almandine (alm). br: bornite with very fine lamellae of chalcopyrite. BSE image. e. Telargpalite (tl) at the contact of magnetite (Mgt) and chalcopyrite (ccp). Note tiny crystals of a Cl-rich ferropargasite (am: up to 3.15 wt.% Cl) enclosed by the chalcopyrite. BSE image. f. Telargpalite (tl) cuts almandine (alm) and fills a fracture in this almandine. There are tiny inclusions of moncheite and tulameenite in this grain of telargpalite. Secondary-electron image.

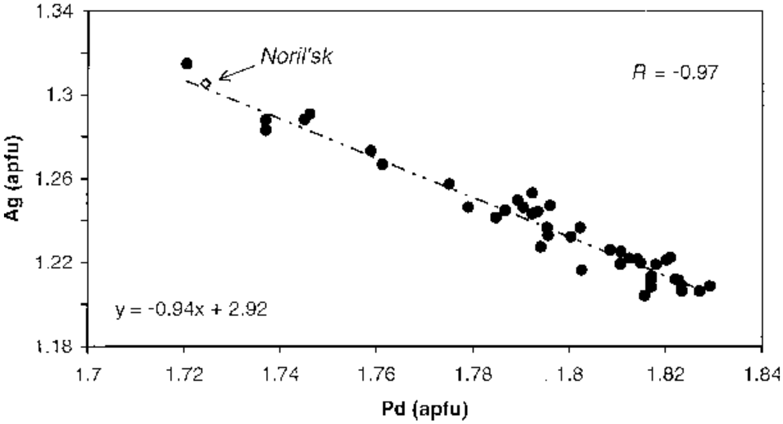

FIG. 5. Correlation between concentrations of Pd and Ag (in atoms per formula unit, *apfu*; basis: Σ atoms = 4) in telargpalite from the Lukkulaisvaara intrusion (filled symbol: WDS data only, this study). Open symbol: telargpalite from Noril'sk (average result of two representative analyses: Genkin *et al.* 1981).

TABLE 6. REFLECTANCE DATA FOR THE UNNAMED Pd–Ag TELLURIDE (Pd_6AgTe_4) FROM LUKKULAISVAARA

λ, nm	R_1 % (air)	R_2 % (air)	R_1 % (oil)	R_2 % (oil)
400	40.1	45.0	29.0	34.2
420	40.3	45.3	29.5	34.3
440	41.7	47.3	31.2	36.6
460	42.8	49.1	33.1	39.1
470	43.2	49.9	34.0	40.1
480	44.0	50.7	35.0	41.4
500	45.1	52.4	36.6	43.3
520	46.8	54.1	38.5	45.2
540	48.5	55.8	40.7	47.1
546	48.8	56.0	41.0	47.5
560	49.9	56.7	42.3	48.2
580	51.3	58.1	43.9	49.8
589	52.0	58.5	44.7	50.2
600	52.7	59.0	45.6	50.8
620	54.1	60.1	46.8	52.0
640	55.1	60.5	47.7	52.5
650	55.6	60.7	48.0	52.7
660	56.2	61.0	48.3	53.1
680	57.2	61.7	49.0	53.5
700	58.2	62.4	49.7	54.1

Spectra obtained with a Zeiss MPM spectrophotometer: WTiC standard (R_{589} in air = 49.5% and R_{589} in oil = 35.5%).

TABLE 7. COLOR VALUES (ILLUMINANT: C) OF UNNAMED Pd–Ag TELLURIDE (Pd_6AgTe_4) FROM LUKKULAISVAARA

		x	*y*	*Y*%	P_e %	λ_d
in air	R_1	0.330	0.333	49.6	10.0	580
	R_2	0.327	0.334	56.4	9.4	577
in oil	R_1	0.340	0.344	41.8	15.6	579
	R_2	0.335	0.342	47.8	13.5	577

Reflectance values are listed in Table 6.

brownish hue to light grayish brown. Its anisotropy is distinct to strong, from light bluish gray to brown. Quantitative measurements of reflectance in air and in oil were performed on a randomly oriented grain (Table 6). The color values of this telluride are listed in Table 7. In addition, reflectance measurements were carried out on another grain of this Pd–Ag telluride, found in the same specimen, and the R_2 (max.) values of this grain are nearly identical to those of the first grain (Table 6).

Figure 6 presents a comparison of the reflectance values (in air) obtained for the unnamed Pd_6AgTe_4 (Table 6) with those of the other Pd–Ag tellurides. Reflectance values of three grains of telargpalite from Noril'sk and Lukkulaisvaara, Russia, (Kovalenker *et al.* 1974, Begizov & Batashev 1981, Cabri 1981) and of three grains of sopcheite from Levack West and Lac-des-Iles, Canada (Dunning *et al.* 1984) were used in this comparison. Sopcheite from the type locality gave a spectrum similar to those of other samples of sopcheite (Dunning *et al.* 1984). In contrast to sopcheite, which has a pronounced anisotropy, telargpalite seems to be optically isotropic.

Telargpalite has higher values of reflectance than sopcheite (Fig. 6), and the unnamed Pd_6AgTe_4 displays the highest reflectance among these tellurides. The existence of a relationship between maximum values of reflectance and chemical composition of these Pd–Ag tellurides is clearly suggested by this comparison. The reflectance values increase with an increase in the proportion of Pd (and decrease in that of Ag) and thus seem to be a function of the atomic Pd:Ag ratio, which equals

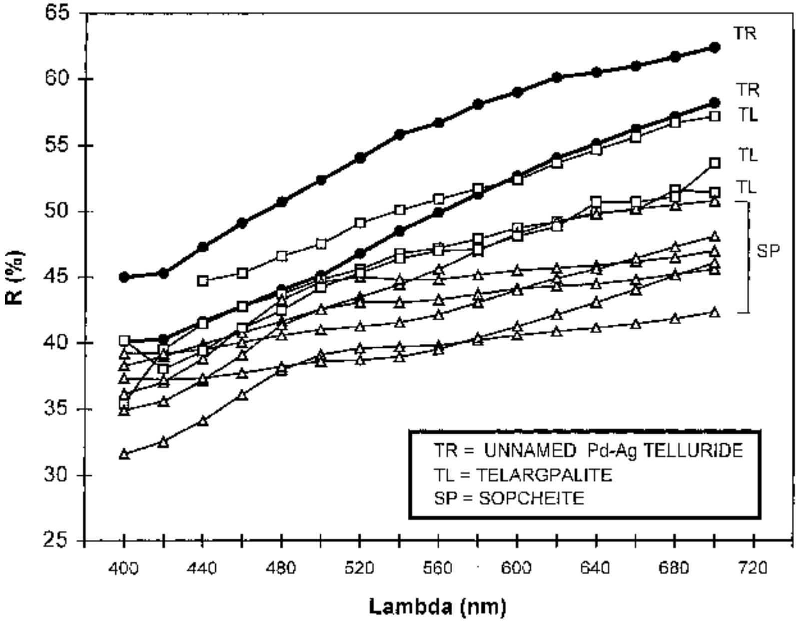

FIG. 6. Comparison of reflectance spectra (measured in air) for unnamed Pd_6AgTe_4 (TR: filled circles and bold curve) with those of other Pd–Ag tellurides reported in the literature. TL (open squares): telargpalite from two localities in Russia (Kovalenker *et al.* 1974, Cabri 1981, Begizov & Batashev 1981). SP (open triangles): sopcheite from two localities in Canada (Dunning *et al.* 1984).

~0.75 for sopcheite, ~1.4 for telargpalite, and ~6 for the unnamed Pd_6AgTe_4.

A range from four indentations, obtained for the unnamed Pd_6AgTe_4 with a Neophot-2 tester (load: 20 g), is 347–369, mean 360 kg/mm^2. An additional measurement was carried out on another grain using a Leitz Durimet tester, and gave a similar result: VHN_{25} = 413 kg/mm^2. The average of these measurements is 371 kg/mm^2.

Composition and formula of the unnamed Pd–Ag telluride

Wavelength-dispersion (WDS) and quantitative energy-dispersion (EDS) methods of electron-microprobe analysis and various facilities, analytical conditions and sets of standards were applied to analyze the unnamed Pd–Ag telluride. Five grains were analyzed. Representative results of these analyses are listed in Table 8; they show that the proportion of Ag in this telluride is nearly invariant (7.5–7.8 wt.%), consistent with results of a previous analysis of this unnamed telluride (7.9 wt.% Ag: Grokhovskaya *et al.* 1992). The results of the WDS and EDS analyses are in good agreement with each other, though the EDS data suggest a somewhat lower content of Pd in this Pd–Ag telluride (Table 8). The unnamed telluride is compositionally very distinct from telargpalite and sopcheite (Fig. 7). The likely ideal formula is Pd_6AgTe_4, which requires an atomic (Pd + Ag) : Te ratio of 1.75. Some extent of Pd-for-Ag substitution

TABLE 8. AVERAGE RESULTS OF ELECTRON-MICROPROBE ANALYSES OF UNNAMED Pd–Ag TELLURIDE FROM LUKKULAISVAARA

No.	Method of analysis	Number of analyses *n*	Pd	Ag	Te	Sum
1	WDS	$n = 17$	52.28	7.54	40.65	100.47
2	WDS	$n = 9$	51.49	7.68	41.03	100.20
3	EDS	$n = 15$	51.00	7.70	41.03	99.73
4	EDS	$n = 5$	51.19	7.83	41.48	100.50
5	–	–	52.12	7.86	40.39	100.37

The analyses that led to composition 1 were carried out using a JEOL–8900 electron microprobe. Pt, Bi, Pb, Se, and As were sought, but not detected (detection limits: Pt 0.07 wt.%, As and Pb 0.05 wt.%, Bi 0.04 wt.%, and Se 0.03 wt.%).
The analyses that led to composition 2 were made with a JEOL–8600 electron microprobe. Bi and Pt were sought, but not detected (detection limits: Pt 0.03 wt.% and Bi 0.02 wt.%).
The analyses that led to compositions 3 and 4 were made with a JEOL JSM–6400 scanning-electron microscope equipped with a LINK eXL energy-dispersion spectrometer.
The conditions of analysis 5 of unnamed Pd–Ag telluride by Grokhovskaya *et al.* (1992) were not specified.
WDS: wavelength-dispersion analyses. EDS: quantitative energy-dispersion analyses.

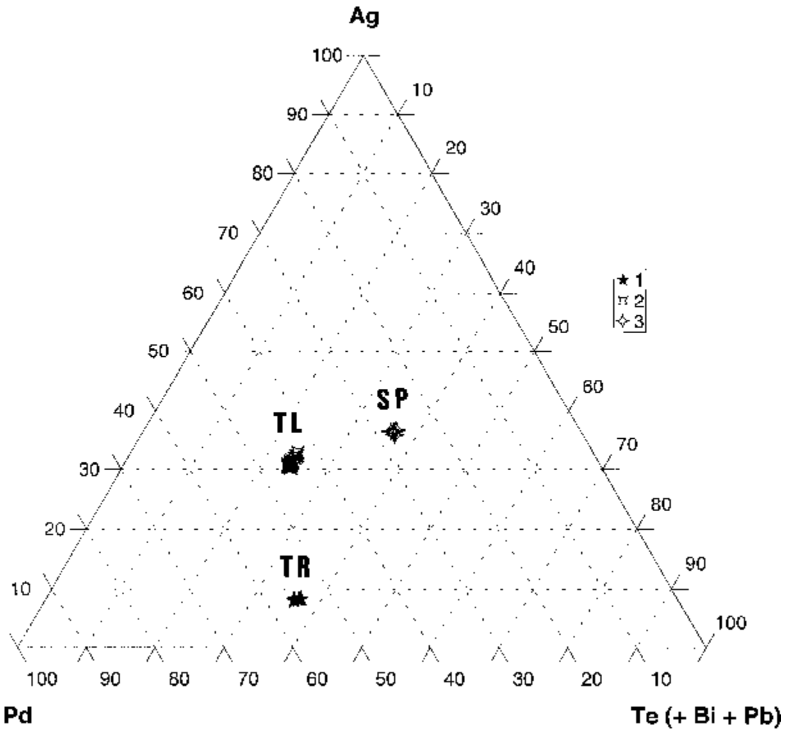

FIG. 7. Compositions of unnamed telluride [Pd_6AgTe_4] (TR: *1*), telargpalite (TL: *2*) and sopcheite (SP: *3*) from the Lukkulaisvaara intrusion in terms of the Pd – Ag – Te (+ Bi + Pb) compositional space (atomic proportions). Telargpalite and the unnamed Pd_6AgTe_4 are from the Nadezhda deposit (this study), and sopcheite is from the Vostok deposit, Lukkulaisvaara intrusion (Barkov & Lednev 1993).

may occur in this telluride, to give $Pd_{6+x}Ag_{1-x}Te_4$ (Table 9). An alternative ideal formula is $Pd_{13}Ag_2Te_9$, which requires the atomic ratio (Pd + Ag) : Te of 1.67; this variant of the formula seems less preferable, though it is not inconsistent with our analytical results.

The compound Pd_6AgTe_4 has been not synthesized so far. A phase having a similar stoichiometry is synthetic Pd_6AgPb_4, whose crystal structure is a homeotype of the filled NiAs structure (Sarah *et al.* 1981).

TABLE 9. COMPOSITION OF THE UNNAMED Pd–Ag TELLURIDE FROM LUKKULAISVAARA, EXPRESSED IN ATOMIC PROPORTIONS

	Σ atoms = 11				Σ atoms = 24		
	Pd	Ag	Σ*Me*	Te	Pd	Ag	Te
1	6.14	0.87	7.01	3.98	13.40	1.91	8.69
2	6.07	0.89	6.96	4.04	13.25	1.95	8.80
3	6.04	0.90	6.94	4.06	13.19	1.96	8.85
4	6.02	0.91	6.93	4.07	13.14	1.98	8.88
5	6.13	0.91	7.04	3.96	13.37	1.99	8.64

The analytical results are listed in Table 8. The atomic proportions are expressed in atoms per formula unit.

THE ASSOCIATION OF Pd–Ag TELLURIDES WITH Cl-RICH AMPHIBOLE AND GARNET

The Cl-rich amphibole

The amphibole associated with the unnamed telluride and telargpalite (*e.g.*, Figs. 4a, b, d, e) corresponds to ferropargasite rich in Cl and Al (Tables 10, 11). The maximum content of Cl in this amphibole reaches 4.5 wt.% Cl (1.24 atoms of Cl per formula unit, *apfu*). Chlorine is distributed quite heterogeneously in these grains, especially in a grain shown in Figure 4b. The content of Cl (WDS data) in this grain ranges from 2.67 to 4.38 wt.%, mean 3.69 wt.% (15 analyses: tugtupite standard), from 2.62 to 4.52 wt.%, mean 3.64 wt.% (29 analyses: KCl standard), and from 1.83 to 4.48 wt.%, mean 3.60 wt.% Cl (16 analyses: sodalite standard). These analytical results are internally consistent. The small crystals of amphibole associated with telargpalite (Fig. 4e) also

TABLE 10. COMPOSITION OF MICRO-INCLUSIONS OF Cl-RICH FERROPARGASITE IN PLATINUM-GROUP MINERALS AT LUKKULAISVAARA

	SiO_2	Al_2O_3	FeO	MnO	MgO	NiO	CaO	Na_2O	K_2O	Cl	O≡Cl	Sum
1	37.55	16.64	17.89	0.08	6.57	0.31	11.03	1.51	1.03	1.88	0.42	94.07
2	37.20	16.28	18.88	0.12	6.46	0.27	11.16	1.72	0.99	2.13	0.48	94.73
3	41.47	17.43	14.29	0.10	8.68	0.25	11.90	1.22	0.54	0.60	0.14	96.34
4	38.12	17.28	17.33	0.10	6.02	0.30	11.08	1.54	1.04	1.79	0.40	94.20
5	38.39	15.94	19.19	0.07	6.40	0.32	11.46	1.72	1.33	2.66	0.60	96.88
6	38.06	14.77	20.52	0.07	6.08	0.32	11.54	1.61	1.71	3.34	0.75	97.27
7	38.64	20.71	17.77	0.09	5.81	0.25	11.71	1.45	1.08	1.66	0.37	98.80
8	38.67	20.80	17.73	0.09	5.67	0.27	11.75	1.39	1.21	1.68	0.38	98.88
9	38.65	20.21	18.37	0.12	5.85	0.31	11.48	1.62	1.10	1.80	0.41	99.10
10	37.85	20.25	18.92	0.12	5.18	0.26	11.54	1.64	1.13	2.16	0.49	98.56
11	36.89	18.30	21.95	0.08	4.59	0.31	11.46	2.01	1.20	3.15	0.71	99.23
12	36.27	18.97	21.40	0.15	4.41	0.30	11.42	1.87	1.18	3.01	0.68	98.30
13	36.50	18.52	21.14	0.16	4.57	0.29	11.54	1.93	1.19	3.08	0.70	98.22
14	37.69	18.97	19.76	0.12	5.75	0.31	11.71	1.79	1.00	2.12	0.48	98.74

Numbers 1–6: micro-inclusions in oulankaite and argentian oulankaite (Figs. 8, 9, 4c). Numbers 7–10: rim at the border of plagioclase and chalcopyrite in immediate contact with oulankaite (Figs. 8, 9). Numbers 11–14: subhedral inclusions in chalcopyrite near telargpalite (Fig. 4e). All Fe is expressed as FeO. Lower totals in some of these compositions reflect the small grain-size. The compositions (in wt.%) were obtained by wavelength-dispersion analyses (JEOL–8900 electron microprobe).

contain a high concentration of Cl, up to 3.15 wt.% (Table 10).

Micro-inclusions of the Cl-rich amphibole in platinum-group minerals

The presence of abundant micro-inclusions of hydrous silicates (dominantly the Cl-rich ferropargasite) in the *BMS*, especially in chalcopyrite (*e.g.*, Figs. 8, 9), and in various *PGM* (*e.g.*, Figs. 3b, 4c, 8, 9), is an important feature of the *PGE* mineralization associated with the pods and stringers at the Nadezhda deposit. Micro-inclusions of amphibole in the *PGM* are characteristically rich in Cl: 0.6 to 3.3 wt.% (anal. 1–6, Table 10).

Two morphological forms of ferropargasite are closely associated with oulankaite (Figs. 8, 9): (1) micro-inclusions, which are partly subhedral, and are particularly numerous in this *PGM* and the host chalcopyrite, and (2) a rim around the oulankaite–(chalcopyrite), which is developed at the contact with a primary plagioclase [$(Ca_{0.67–0.68}Na_{0.30–0.34}Fe_{0.02}K_{0.01})_{\Sigma 1.01–1.04}Si_{2.28–2.29}Al_{1.71}O_8$: results of two WDS analyses). The micro-inclusions have a composition similar to that of the rim of amphibole (*cf.*, anal. 2 and 10, Table 10), suggesting similar conditions of crystallization and a late-stage formation for this mineral association.

Composition and element correlations

The Al–Cl-rich amphibole that occurs in various textural associations in the Nadezhda deposit is ferropargasite and its Cl-dominant analogue, which thus could well be a new mineral. The WDS analyses reveal a strong variation in Cl (*e.g.*, Table 11) and covariations in the content of Cl and of Fe and K. The correlation between Cl and FeO (wt.%) is positive and strong (Fig. 10). The analytical results listed in Table 11 show the existence of strong positive correlations: Cl–Fe (correlation coefficient R = 0.90), Cl–K (R = 0.86), and Cl–^{IV}Al (R = 0.76).

The garnet that occurs in a close textural relationship with the Pd–Ag tellurides (Figs. 4a, f) is almandine (Table 12), whose composition is similar to other examples of garnet from the Nadezhda deposit (Barkov *et al.* 1999).

DISCUSSION AND CONCLUSIONS

Composition and maximum reflectance of the Pd–Ag tellurides

Our observations (Fig. 6) suggest the existence of a relationship between the composition and maximum reflectance value of the Pd–Ag tellurides. A decrease in the content of Ag and a complementary increase in Pd accompanies an increase in the maximum value of reflectance.

Substitution relationships of Pd and Ag in the Pd–Ag tellurides

The empirical formulae of telargpalite $Pd_{2–x}Ag_{1+x}(Te,Bi,Pb)$, where $0 < x < 0.3$, and the unnamed $Pd_{6+x}Ag_{1–x}Te_4$ ($0 \leq x \leq 0.15$) suggest that isomorphous substitution involving Pd and Ad exists in these Pd–Ag tellurides. Limited Ag-for-Pd substitution likely occurs in telargpalite, as is indicated by the strong negative

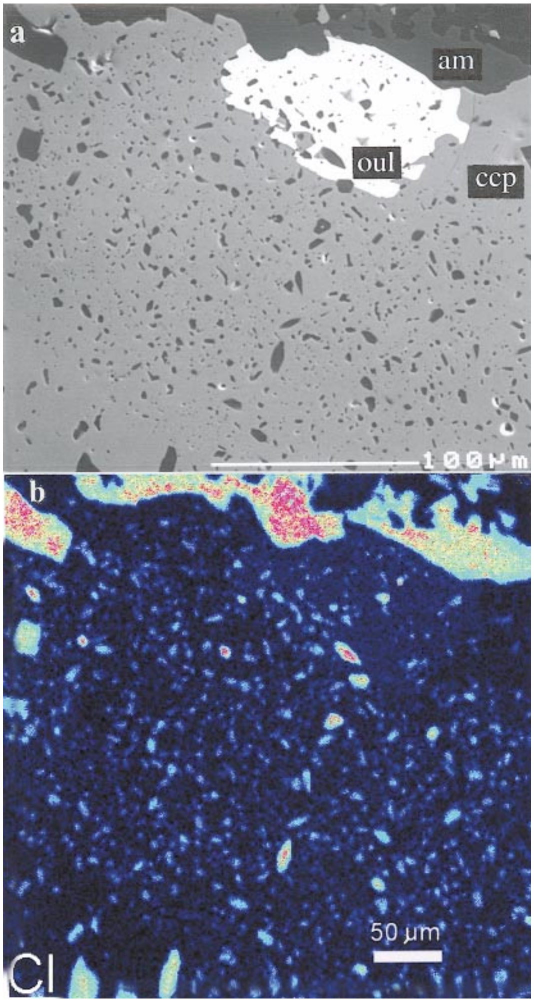

FIG. 8. a. Numerous tiny inclusions of a Cl-rich ferropargasite (dark gray) in chalcopyrite (ccp) and oulankaite (oul). Amphibole rich in Cl also occurs as a rim (am) along the contact between chalcopyrite –(oulankaite) and a primary plagioclase ($An_{65.7–68.7}Ab_{30.3–33.3}Or_{1.0}$). Secondary-electron image. b. X-ray map for chlorine (Cl) over part of the same area as in Figure 8a, showing the presence of Cl in the microcrystalline amphibole and in the rim of amphibole.

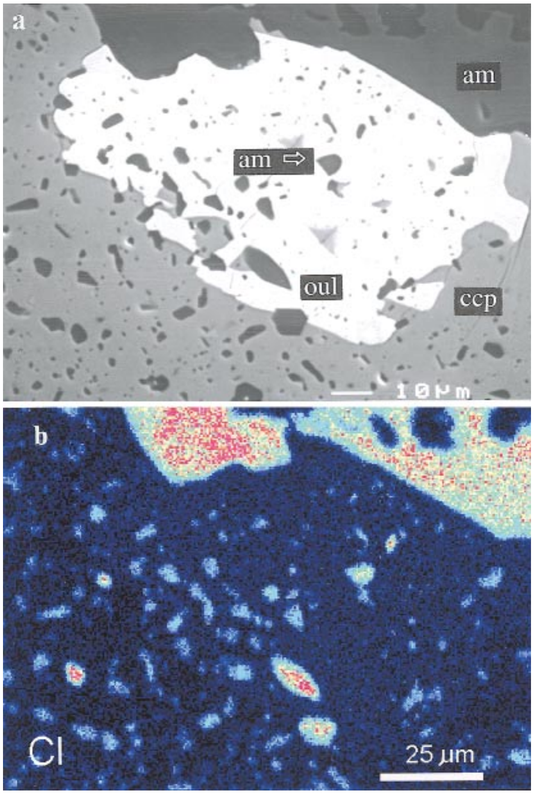

FIG. 9. a. Micro-inclusions of Cl-rich ferropargasite (am: 1.8–2.1 wt.% Cl) in oulankaite (oul: white); magnification of the grain shown in Figure 8a. Secondary-electron image. The rim of amphibole (am) in immediate contact with the oulankaite–(chalcopyrite) contains approximately the same level of Cl (1.7–2.2 wt.% Cl) as the micro-inclusions. ccp: chalcopyrite. b. X-ray map for chlorine (Cl) of part of the area shown in Figure 9a, indicating the presence of Cl in the microcrystalline amphibole, including submicrometric (1–2 µm) inclusions in the oulankaite.

correlation between the concentrations of Pd and Ag (Fig. 5). Limited Pd-for-Ag substitution also likely occurs in the unnamed Pd_6AgTe_4 (Table 9).

Textural relations of the telargpalite and almandine

The textural relationships documented here clearly imply the late crystallization of the Pd–Ag tellurides in the Nadezhda deposit (Figs. 3a, b, 4a–f). Temperature of equilibration of the almandine – Cl-rich pargasite – staurolite assemblage at Nadezhda, estimated on the basis of calibrations for the garnet–hornblende and garnet–staurolite equilibria, ranges from *ca.* 560 to 670° C (Barkov *et al.* 1999). The grain of telargpalite that cuts almandine (Fig. 4f) seems to have crystallized at a temperature lower than that at which the almandine and the associated Al-rich secondary minerals achieved equilibrium. Signs of the replacement of moncheite by telargpalite, which are quite commonly observed in this deposit (Figs. 3b, c), also agree well with the rather late crystallization of telargpalite.

TABLE 11. COMPOSITION OF THE Cl-RICH FERROPARGASITE ASSOCIATED WITH THE UNNAMED Pd–Ag TELLURIDE AT LUKKULAISVAARA

	SiO_2	Al_2O_3	FeO	MnO	MgO	NiO	CaO	Na_2O	K_2O	Cl	H_2O	O≡Cl	Sum
1	38.34	16.37	22.05	0.18	5.51	0.33	11.80	1.82	0.80	2.67	1.25	0.60	100.52
2	35.94	16.73	23.66	0.16	4.13	0.36	11.62	1.93	1.00	3.83	0.89	0.86	99.19
3	36.02	16.11	23.14	0.19	4.36	0.37	11.53	2.04	1.14	3.89	0.86	0.88	98.77
4	35.50	16.34	23.72	0.17	4.12	0.15	11.79	1.89	1.11	4.04	0.82	0.91	98.74
5	36.11	15.13	23.44	0.14	4.32	0.35	11.63	2.01	1.17	4.32	0.73	0.97	98.38
6	34.99	16.82	22.68	0.16	4.02	0.43	11.55	1.94	1.12	4.38	0.71	0.99	97.81
7	35.95	15.28	24.17	n.a.	4.37	0.34	11.36	2.10	1.20	3.62	0.92	0.82	98.49
8	36.83	15.93	22.46	n.a.	5.08	0.35	11.50	2.01	0.94	3.41	1.00	0.77	98.74
9	34.85	16.81	24.31	0.26	4.06	0.42	11.40	2.05	1.08	4.06	0.81	0.92	99.19
10	37.41	15.64	22.36	0.23	5.17	0.28	11.64	2.02	1.05	3.48	1.00	0.79	99.49
11	37.40	16.78	21.48	0.20	5.63	0.26	11.65	1.88	1.03	3.04	1.13	0.69	99.79
12	35.04	16.23	23.84	0.21	4.12	0.26	11.47	2.10	1.19	4.48	0.69	1.01	98.62
13	39.12	16.58	19.68	0.16	6.73	0.31	11.96	1.79	0.66	1.83	1.48	0.41	99.89
14	36.60	15.09	23.79	0.19	4.69	0.29	11.58	2.10	1.26	3.94	0.86	0.89	99.50
15	36.07	16.43	23.87	0.24	4.47	0.28	11.57	2.07	1.33	4.00	0.85	0.90	100.28

	Si	^{IV}Al	^{VI}Al	Fe	Mn	Mg	Ni	Ca	Na	K	Cl	OH
1	5.974	2.026	0.981	2.873	0.024	1.279	0.041	1.970	0.550	0.159	0.705	1.295
2	5.795	2.205	0.976	3.191	0.022	0.993	0.021	2.008	0.603	0.206	1.047	0.953
3	5.838	2.162	0.917	3.137	0.026	1.053	0.048	2.003	0.641	0.236	1.069	0.931
4	5.778	2.222	0.913	3.229	0.023	0.999	0.020	2.056	0.596	0.230	1.114	0.886
5	5.908	2.092	0.827	3.207	0.019	1.053	0.046	2.039	0.638	0.244	1.198	0.802
6	5.743	2.257	0.997	3.113	0.022	0.983	0.057	2.031	0.617	0.235	1.218	0.782
7	5.869	2.131	0.809	3.300	-	1.063	0.045	1.987	0.665	0.250	1.001	0.999
8	5.910	2.090	0.923	3.014	-	1.215	0.045	1.977	0.625	0.192	0.927	1.073
9	5.674	2.326	0.901	3.310	0.036	0.985	0.055	1.989	0.647	0.224	1.120	0.880
10	5.959	2.041	0.895	2.979	0.031	1.227	0.036	1.987	0.624	0.213	0.939	1.061
11	5.885	2.115	0.998	2.827	0.027	1.320	0.033	1.964	0.574	0.207	0.811	1.189
12	5.743	2.257	0.879	3.268	0.029	1.006	0.034	2.014	0.667	0.249	1.244	0.756
13	6.022	1.978	1.031	2.534	0.021	1.544	0.038	1.973	0.534	0.130	0.477	1.523
14	5.911	2.089	0.784	3.213	0.026	1.129	0.038	2.004	0.658	0.260	1.078	0.922
15	5.781	2.219	0.886	3.200	0.033	1.068	0.036	1.987	0.643	0.272	1.087	0.913

Numbers 1–9: the analyses were done with a JEOL–733 microprobe. The concentration of Cl was established using tugtupite (SPI Supplies: anal. 1–6) and KCl (anal. 7–9) as standards. Numbers 10–15: the analyses were done with a JEOL–8600 microprobe. The concentration of Cl was established using sodalite as a standard. F was sought, but not detected (detection limit: 0.1 wt.% F). All Fe is expressed as FeO. H_2O (wt.%) was calculated on the basis of charge balance. Formulae were calculated on the basis of (O – OH + Cl) = 24. n.a.: not analyzed. The grains analyzed are shown in Figures 4a, d. The compositions (in wt.%) were obtained by wavelength-dispersion analyses.

Implications for the existence of a Cl-rich environment

The sill-like body of microgabbronorite in the Lukkulaisvaara intrusive complex seems to have crystallized rather rapidly, resulting in the fine-grained and locally microgranular textures. The extent of concentration of magmatic volatiles in the body may have varied significantly, producing the mineralized pods and stringers of the coarse-grained to pegmatitic mafic rocks associated with the microgabbronorite.

The Pd–Ag tellurides occur in association with an unusual assemblage of the Al-rich secondary minerals in the Nadezhda *PGE* deposit, which includes the microcrystalline staurolite, Cl-rich ferropargasite, almandine, among others (Table 1). These secondary minerals are considered to have formed by local reactions involving the breakdown of the primary plagioclase and enstatite in a hydrous environment at a deuteric (postmagmatic-hydrothermal) stage of crystallization (Barkov *et al.* 1999). The presence of trace corundum is consistent with the leaching and ultimate loss of Ca, Na and other elements *via* the fluid phase.

The high concentration of Cl in the ferropargasite in the *PGE*-rich pods and stringers indicates that Cl has been an important component of a hydrous fluid in the deuteric environment. The intergrowth relationship of the Pd–Ag tellurides with such a Cl-rich amphibole (up to 4.5 wt.% Cl), and the presence of the abundant micro-inclusions of the Cl-rich ferropargasite in the *PGM* (*e.g.*, Figs. 4a–f, 8, 9), suggest that these *PGM* precipitated from (or were remobilized by) the heated brine.

The positive correlations between Cl and Fe, Cl and K, and Cl and ^{IV}Al in the compositions of the Cl-rich ferropargasite at Nadezhda are indicative of a structural control for the incorporation of Cl in the crystal structure, consistent with the crystal-chemical findings of Oberti *et al.* (1993). The maximum concentration of Cl

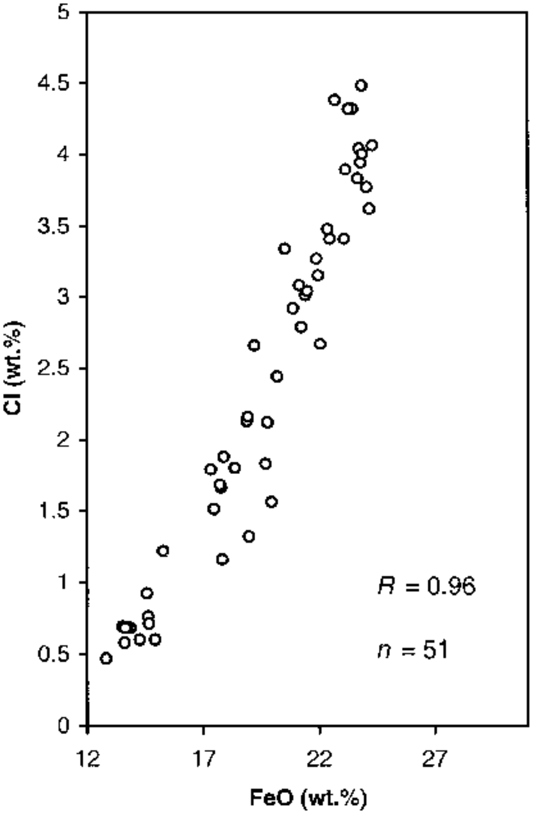

FIG. 10. Correlation between contents of Cl and FeO (in wt.%) in Cl-rich amphibole from coarse-grained (*PGE*-rich) gabbronorite, Nadezhda deposit, Lukkulaisvaara intrusion.

TABLE 12. COMPOSITION OF GARNET ASSOCIATED WITH Pd–Ag TELLURIDES AT LUKKULAISVAARA

No.	*1*	*2*		*1*	*2*
SiO_2 wt.%	38.80	38.02	Si *apfu*	6.03	6.03
TiO_2	0.03	0.04	^{IV}Al	-	-
Al_2O_3	21.85	21.19	^{VI}Al	4.00	3.96
Cr_2O_3	0.04	n.d.	Fe	3.52	3.80
FeO	27.06	28.67	Mg	1.20	0.45
MnO	2.08	4.77	Mn	0.27	0.64
MgO	5.16	1.89	Ca	0.94	1.11
NiO	<0.01	<0.01	K	<0.01	<0.01
CaO	5.64	6.51	Na	-	-
Na_2O	n.d.	n.d.	Ni	-	-
K_2O	0.02	0.01	Cr	<0.01	-
			Ti	<0.01	<0.01
Sum	100.68	101.10			

Column 1: almandine shown in Figure 4f. Column 2: almandine shown in Figure 4a. Results of wavelength-dispersion analyses (JEOL–8900 microprobe). All Fe is expressed as FeO. The number of cations was calculated on the basis of 24 atoms of oxygen per formula unit (*apfu*).

in the amphibole from Nadezhda is higher than that reported for amphiboles from most of other *PGE* deposits in the Bushveld and Sudbury complexes (Ballhaus & Stumpfl 1986, Springer 1989, Li & Naldrett 1993, Watkinson 1994). McCormick & McDonald (1999) have recently reported the occurrence of amphibole having a comparable content of Cl (4 wt.%), from the Fraser mine of the Sudbury complex.

The source of the Cl

Nearly end-member chlorapatite was observed to be an abundant intercumulus phase in ultramafic cumulates of the Lukkulaisvaara intrusion (Barkov *et al.* 1995a). In addition, intercumulus apatite is present in various mafic rocks of the layered series at Lukkulaisvaara and contains an elevated concentration of Cl (1.1 to 4.1 wt.% Cl: Barkov *et al.*, unpubl. data). These observations seem to be consistent with a primary magmatic source of the Cl and indicate a relative enrichment in Cl in the intercumulus liquid at a postcumulus stage of crystallization of the intrusion.

We suggest that an initial enrichment in Cl may have occurred during crystallization of the sill-like body, in isolated volumes of the remaining volatile-saturated magma, from which the *PGE*-rich coarse-grained gabbronorite crystallized. A subsequent enrichment in Cl likely occurred at a postmagmatic stage of crystallization of the coarse-grained pods and stringers, and gave rise to various textural manifestations of the Cl-rich ferropargasite associated with the *PGM*.

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