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MENSHIKOVITE, $Pd_3Ni_2As_3$, A NEW PLATINUM-GROUP MINERAL SPECIES FROM TWO LAYERED COMPLEXES, RUSSIA

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Abstract

Menshikovite, ideally $Pd_3Ni_2As_3$, is a new mineral species found in two localities in Russia. It occurs in a pod of coarse-grained, entirely altered gabbronorite rich in sulfides (up to 30 vol.%), hosted by a microgabbronorite, in the Vostok deposit, Lukkulaisvaara intrusion, in Karelia. There, menshikovite (up to 0.2 mm) is associated with chalcopyrite, pentlandite, calcic amphibole (mostly actinolite), clinochlore, merenskyite, kotulskite, sobolevskite, michenerite, hollingworthite, hessite, and a Re-rich sulfide. Menshikovite (up to 0.1 mm) also occurs in mineralized quartz–feldspar sandstones, which are metasomatically altered and recrystallized. They are located at the lower (exo)-contact of the Chiney intrusion in Siberia, and contain amphibole(s), mica(s), chlorite, disseminated or massive sulfides (mostly chalcopyrite), Pd-rich maucherite, nickeline, sperrylite, mertieite-II or stibiopalladinite (or both), isomertieite, majakite, and michenerite. We also report a third occurrence of menshikovite from the Oktyabr' deposit, Noril'sk complex, in Siberia. In reflected light, menshikovite is pink and opaque. A cleavage is not observed. There is no evidence of bireflectance. The anisotropy is weak, from light gray to brownish gray. Reflectance percentages in air (and in oil) are, for R_1 and R_2, at 470 nm 48.4, 50.2 (38.45, 39.3), at 546 nm 51.2, 53.2 (41.0, 41.8), at 589 nm 53.2, 55.3 (42.3, 43.3), and at 650 nm 56.6, 58.7 (46.6, 47.8). Fine twins are present. The average value of microhardness $VHN_{40, 50, 65}$ is 517.1 kg/mm^2; it has Mohs hardness of ~5 and is brittle. The average of two sets of multiple wavelength-dispersion electron-microprobe analyses of menshikovite from Lukkulaisvaara gave Pd 48.18, Pt 0.07, Ni 17.77, Fe 0.07, As 33.91, the total is 100.0 wt.% (not normalized), corresponding to $Pd_{2.99}(Ni_{2.00}Fe_{0.01})_{\Sigma 2.01}As_{2.99}$ (basis: Σ atoms = 8). Compositions of menshikovite from Chiney vary from $Pd_{3.00}(Ni_{1.98}Co_{0.01})_{\Sigma 1.99}As_{2.99}$ to $Pd_{3.15}(Ni_{1.97}Co_{0.01})_{\Sigma 1.98}As_{2.86}$. A solid-solution series probably exists between menshikovite and majakite [*i.e.*, $(Pd,Ni)_2As$ of the β-Pd_2As type]. The powder pattern of menshikovite from Lukkulaisvaara was indexed on a hexagonal cell with *a* 8.406(4), *c* 6.740(4) Å, and *V* 412.4(6) Å^3. The strongest eight lines in this pattern [*d* in Å (I)(*hkl*)] are 2.626(10)(112), 2.477(10)(202), 2.429(8)(300), 2.283(7)(301), 2.150(6)(103), 1.978(7)(113), 1.818(7)(400) and 1.757(6)(401). *Menshikovite* formed in volatile-rich environments relatively late in the crystallization history of the layered complexes. The name honors Yurii P. Men'shikov, of the Kola Science Center, Apatity, Russia.

Keywords: menshikovite, new mineral species, Pd–Ni–As system, arsenide, platinum-group mineral, platinum-group elements, layered intrusion, mafic–ultramafic rocks, Lukkulaisvaara, Chiney, Noril'sk, Russia.

Sommaire

La menshikovite, dont la formule idéale est $Pd_3Ni_2As_3$, est une nouvelle espèce minérale découverte en deux endroits en Russie. Elle se présente dans une lentille de gabbronorite à gros grains, entièrement altérée, riche en sulfures (jusqu'à 30% en volume), et encaissée par une microgabbronorite dans le gisement de Vostok, complexe de Lukkulaisvaara, en Karélie. La menshikovite, qui atteint une taille de 0.2 mm, y est associée à chalcopyrite, pentlandite, amphibole calcique (surtout actinolite), clinochlore, merenskyite, kotulskite, sobolevskite, michenerite, hollingworthite, hessite, et un sulfure riche en Re. La menshikovite (jusqu'à 0.1 mm de taille) se présente aussi dans des grès à quartz–feldspath minéralisés, modifiés par métasomatose et recristallisés. Ces roches sont situées près du contact externe inférieur du massif intrusif de Chiney, en Sibérie, et contiennent

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amphibole(s), mica(s), chlorite, sulfures disséminés ou massifs (surtout la chalcopyrite), maucherite palladifère, nickeline, sperrylite, mertieïte-II ou stibiopalladinite (ou les deux), isomertieïte, majakite, et michenerite. Nous décrivons aussi un troisième indice de menshikovite provenant du gisement de Oktyabr', complexe de Noril'sk, en Sibérie. En lumière réfléchie, le minéral est rose et opaque. Il ne semble pas y avoir de clivage, et aucune biréflectance n'est évidente. L'anisotropie est faible, de gris pâle à gris brunâtre. Les valeurs de réflectance dans l'air (et dans l'huile), pour R_1 et R_2, sont: à 470 nm, 48.4, 50.2 (38.45, 39.3), à 546 nm, 51.2, 53.2 (41.0, 41.8), à 589 nm, 53.2, 55.3 (42.3, 43.3), et à 650 nm, 56.6, 58.7 (46.6, 47.8). De fines macles sont présentes. En moyenne, la microdureté $VHN_{40, 50, 65}$ est 517.1 kg/mm^2; la dureté de Mohs est d'environ 5, et il est assez cassant. Deux groupes d'analyses à la microsonde électronique, obtenues en dispersion de longueurs d'ondes, indiquent que la menshikovite de Lukkulaisvaara contient Pd 48.18, Pt 0.07, Ni 17.77, Fe 0.07, As 33.91, pour un total de 100.0% par poids (non normalisé), correspondant à $Pd_{3.00}(Ni_{2.00}Fe_{0.01})_{\Sigma 2.01}As_{2.99}$ (Σ atomes = 8). Les compositions de la menshikovite de Chiney varient entre $Pd_{3.00}(Ni_{1.98}Co_{0.01})_{\Sigma 1.99}As_{2.99}$ et $Pd_{3.15}(Ni_{1.97}Co_{0.01})_{\Sigma 1.98}As_{2.86}$. Une solution solide existerait entre la menshikovite et la majakite [*i.e.*, $(Pd,Ni)_2As$ du type structural β-Pd_2As]. Le spectre de diffraction X (méthode des poudres) de la menshikovite de Lukkulaisvaara a été indexé sur une maille hexagonale, *a* 8.406(4), *c* 6.740(4) Å, et *V* 412.4(6) Å^3. Les huit raies les plus intenses [*d* en Å (I)(*hkl*)] sont: 2.626(10)(112), 2.477(10)(202), 2.429(8)(300), 2.283(7)(301), 2.150(6)(103), 1.978(7)(113), 1.818(7)(400) et 1.757(6)(401). La menshikovite s'est formée dans un milieu enrichi en phase volatile et serait relativement tardive dans l'évolution des complexes stratiformes. Le nom honore Yurii P. Men'shikov, du Centre scientifique de Kola, à Apatity, en Russie.

(Traduit par la Rédaction)

Mots-clés: menshikovite, nouvelle espèce minérale, système Pd–Ni–As, arséniure, minéral du groupe du platine, éléments du groupe du platine, intrusion stratiforme, roches mafiques–ultramafiques, Lukkulaisvaara, Chiney, Noril'sk, Russie.

INTRODUCTION

In this paper, we describe the properties of menshikovite, which is a new species of platinum-group mineral (*PGM*) discovered in two mafic-ultramafic layered complexes in Russia. These complexes are Lukkulaisvaara in northern Russian Karelia and Chiney in the Chita region, southeastern Siberia (Fig. 1). In addition, we document here a solid solution that may be important in menshikovite and report the occurrence of menshikovite in the Oktyabr' Cu-Ni-platinum-group element (*PGE*) deposit of the Noril'sk complex, northern Siberia, Russia.

The mineral name *menshikovite* (меньшиковит in Cyrillic) is chosen to honor Dr. Yurii P. Men'shikov (Юрий Павлович Меньшиков) (b. 1934), research scientist at the Geological Institute of the Kola Science Center, Russian Academy of Sciences, in Apatity, in recognition of his important contributions to mineralogy. Thirty-eight new mineral species (*i.e.*, about 1% of the total number of valid species) have been discovered by Yu.P. Men'shikov and his coworkers. The new mineral and its name have been approved prior to publication by the IMA Commission on New Minerals and Mineral Names. A polished section containing menshikovite from the Lukkulaisvaara intrusion has been deposited in the Fersman Museum, Moscow.

There is an incompletely characterized arsenide of Pd and Ni, synthesized by Gervilla *et al.* (1994), which is very close to menshikovite in composition (Barkov *et al.* 2000). This synthetic arsenide probably is menshikovite, as also are unnamed Pd–Ni arsenides reported from the Stillwater (Cabri *et al.* 1975) and Coldwell complexes (Mulja & Mitchell 1990).

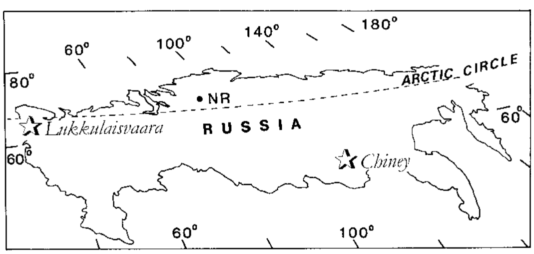

FIG. 1. Location of the Lukkulaisvaara and Chiney layered intrusions (shown by stars) and of the Noril'sk complex (NR) in Russia.

OCCURRENCES AND ASSOCIATED MINERALS

The Lukkulaisvaara intrusion

The Lukkulaisvaara layered complex, of Early Proterozoic age (*ca.* 2.4 Ga), consists mostly of various gabbronorites and subordinate olivine-rich cumulates, which are present at a lower stratigraphic level (*e.g.*, Glebovitsky *et al.* 2001). Major zones of the *PGE* mineralization are controlled by sill-like or dike-like bodies of microgabbronorite, which are hosted by mafic rocks of the layered series of the complex. The mineralized pods and stringers of coarse-grained to pegmatitic mafic rocks (less than 0.5 m in size) are associated with the microgabbronorite bodies at the *Nadezhda* (Begizov & Batashev 1981, Barkov *et al.* 1995, 1996b, 2001) and *Vostok* (Barkov *et al.* 1996a) deposits. The rocks of these pods and stringers are altered to various extents; they are enriched in base-metal sulfides and are rich in the *PGE*, especially in Pd and, to a lesser extent, Pt.

Menshikovite was discovered in a mineralized pod of coarse-grained, entirely altered gabbronorite, associated with a microgabbronorite at the *Vostok* (*East*) deposit in the eastern part of the Lukkulaisvaara intrusion. The gabbronorite is strongly enriched in disseminated base-metal sulfides (up to 30 vol.%), dominantly chalcopyrite, pentlandite, and violarite, which is a product of replacement of the primary pentlandite. This rock is rich in Pd (10.5 ppm), Ag (24 ppm), and Pt (2.9 ppm). It is composed of varying proportions of calcic amphibole (mostly actinolite) and clinochlore, which both have highly magnesian compositions. Their average *Mg#* index [*Mg#* = 100Mg / (Mg+Fe+Mn)] is 84.2 (results of eight quantitative wavelength-dispersion, WDS, electron-microprobe analyses) and 74.5 (two WDS electron-microprobe analyses), respectively. Similar levels of the *Mg#* are characteristic of actinolite and clinochlore, also the main hydroxyl-bearing silicates in the unusually *PGE*-rich, nearly sulfide-free Kirakkajuppura deposit in the neighboring Penikat layered intrusion, Finland (Barkov *et al.* 1999a). The main *PGM* at the Vostok deposit are merenskyite, members of the kotulskite – sobolevskite series and michenerite. These *PGM* commonly occur as intergrowths up to 0.2 mm in size, which also include hessite. Unusual and rare minerals occur in the Vostok deposit, such as an unnamed sulfide of Re, Mo and Cu [$(Cu,Fe)(Re,Mo)_4S_8$], hollingworthite that contains a very high concentration of Os (up to 11.6 wt.%), and a rhodian cobaltite–gersdorffite associated with this hollingworthite (Barkov & Lednev 1993, Barkov *et al*. 1996a). The other ore minerals in the Vostok deposit are listed in Table 1.

TABLE 1. ORE MINERALS ASSOCIATED WITH MENSHIKOVITE IN THE LUKKULAISVAARA AND CHINEY LAYERED COMPLEXES, RUSSIA

Lukkulaisvaara	Chiney	
Disseminated mineralization	Disseminated mineralization	Massive mineralization
Chalcopyrite	Chalcopyrite	Chalcopyrite
Pentlandite	Bornite	Cobaltite–gersdorffite
Violarite	Ilmenite	Maucherite (Pd-rich)
Sphalerite	Cobaltite–gersdorffite	Nickeline
Molybdenite	Maucherite (Pd-rich)	Sperrylite
Merenskyite	Nickeline	Isomertieite
Kotulskite	Sperrylite	Paolovite (As-rich)
Sobolevskite	Majakite	Hollingworthite
Michenerite	Mertieite-II or stibiopalladinite	Au–Ag alloy
Hollingworthite (Os-rich)	Michenerite	
Sopcheite	Au–Ag alloy	
Stibiopalladinite or mertieite		
Paolovite (As-rich)		
Cobaltite–gersdorffite (Rh-rich)		
Hessite		
Argentopentlandite		
$Pd_2(Sn,Sb)$		
$(Cu,Fe)(Re,Mo)_4S_8$		

Menshikovite typically forms anhedral grains associated with chalcopyrite and pentlandite (Figs. 2A, B). Their grain-size ranges from <5 μm to *ca.* 0.2 mm in the longest dimension. In many instances, the grains of menshikovite occur in immediate contact with hydrous silicates (Figs. 2A, B). In addition, a thin veinlet, or a veinlet-like grain of menshikovite, was observed transecting a hydrous silicate (Fig. 2C). Merenskyite rich in Bi and members of the sobolevskite–kotulskite series (also Bi-rich) may occur as tiny inclusions in (or as minute grains attached to) menshikovite (Fig. 2A).

The Chiney intrusion

The Chiney layered lopolith (~17 km across) is located in the Kodar–Udokan horst, western Aldan Shield (Konnikov 1986, Gongal'skii & Krivolutskaya 1993). This intrusion is Proterozoic in age (~1.7 Ga?) (Konnikov 1986, and references therein). The Chiney complex consists of interlayered gabbro, gabbronorite, anorthosite and pyroxenite. In addition, layers of rocks enriched in titaniferous magnetite are present in the lower part of the complex. Rocks of two types were observed in the contact zone of the Chiney intrusion. (1) The "endocontact" rocks mostly consist of quartz monzogabbro, monzonite, and melanogranite. (2) The "exocontact" rocks are mostly quartz–feldspar sandstones of the Early Proterozoic Udokan series, which are characterized by a high content of K-feldspars (13 to 24 vol.%: Konnikov *et al.* 1981), and are metasomatically altered and recrystallized to various extents.

Zones of Pd-rich mineralization are associated with base-metal sulfides at the lower contact of the Chiney intrusion with the quartz–feldspar sandstones. Menshikovite was discovered in heavy-mineral concentrates, obtained from samples of mineralized quartz–feldspar sandstones, which are metasomatically altered, recrystallized or hornfelsed. These samples were collected in the exocontact zone in the eastern part of the intrusion, where extensive recrystallization of the sandstones resulted in the appearance of coarser-grained rocks with a granoblastic texture. These rocks contain disseminated or massive sulfide mineralization enriched in chalcopyrite. The major minerals in the mineralized rocks are micas (mainly biotite plus minor muscovite), amphibole and chlorite, which together commonly account for more than 50 vol.% of the rock.

The ore minerals identified in the heavy-mineral concentrates in association with menshikovite are listed in Table 1. Pd-bearing maucherite, nickeline and menshikovite were observed (mostly in separate grains and rarely in mutual intergrowths) in samples of the heavy-mineral concentrates obtained from the zones containing both massive and disseminated sulfide mineralization. In addition, Pd-bearing maucherite, menshikovite and majakite were observed in samples of the heavy-mineral concentrates obtained from the zones containing disseminated mineralization. Results of electron-microprobe analyses (WDS) indicate that maucherite contains up to 2.1 at.% Pd (*i.e.*, 3.3 wt.% Pd), and the average content of Pd in the maucherite is 1.26 wt.% (mean of twenty WDS electron-microprobe analyses: this study). In contrast, nickeline, which is less abundant, is devoid of Pd.

Sperrylite and antimonides of Pd are the most common *PGM* in this deposit. These antimonides are mertieite-II (or stibiopalladinite, or both) associated with the disseminated mineralization and isomertieite associated with the massive mineralization. Majakite and michenerite are rare. In the exocontact zone of the Chiney complex, unusual oxide minerals of Pd, Sb and Bi also are present in association with base-metal sulfides (Tolstykh *et al.* 2000).

Menshikovite typically occurs in association with massive sulfide mineralization (Table 1), and only a few grains of menshikovite were found in association with the disseminated mineralization. A total of twenty-six grains of menshikovite (10 μm to 0.1 mm in size) were found in the heavy-mineral concentrates. The seventeen grains are complex intergrowths of menshikovite with

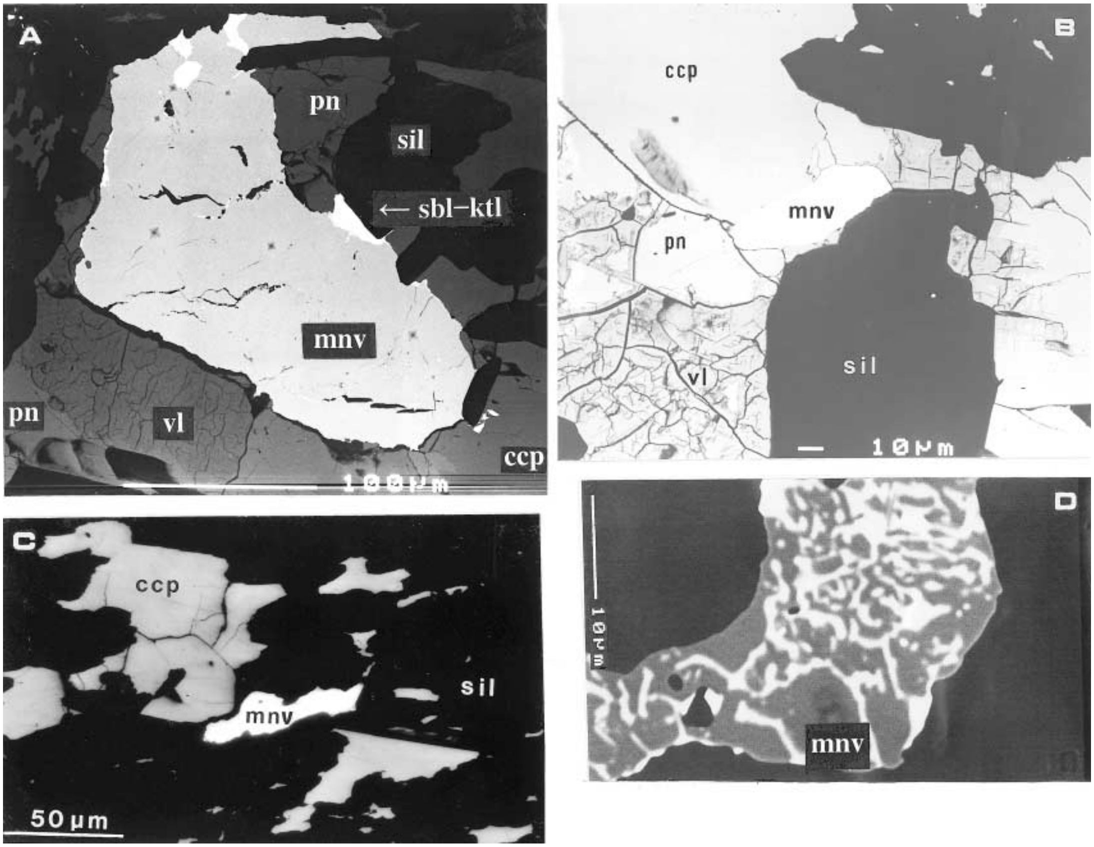

Fig. 2. A. A large grain of menshikovite (mnv) from the Lukkulaisvaara intrusion. The associated minerals are pentlandite (pn), chalcopyrite (ccp), a member of the violarite–greigite series, vl, $[(Ni_{1.65}Fe_{1.36}Co_{0.03})_{\Sigma 3.04}S_{3.96}]$, which is secondary after the pentlandite $[(Ni_{4.85}Fe_{4.08}Co_{0.07})_{\Sigma 9.00}S_{7.99}]$, and a hydrous silicate (sil: a calcic amphibole). Tiny inclusions of members of the sobolevskite–kotulskite series (sbl-ktl) $[Pd_{1.0}(Bi_{0.52\text{-}0.61}Te_{0.44\text{-}0.53})]$ and a Bi-rich merenskyite occur at the contact of the menshikovite grain. B. A grain of menshikovite (mnv), which is located at the contact of chalcopyrite (ccp), pentlandite (pn) and a hydrous silicate (sil: a calcic amphibole) from Lukkulaisvaara. A member of the violarite–greigite series, vl, $[(Ni_{1.83}Fe_{1.17})_{\Sigma 3.00}S_{4.00}]$ is secondary after the pentlandite $[(Ni_{4.61}Fe_{4.37})_{\Sigma 8.98}S_{8.01}]$. C. A veinlet-like grain of menshikovite (mnv) located among hydrous silicates (sil: calcic amphibole and clinochlore) from Lukkulaisvaara. ccp is chalcopyrite. D. A composite grain of menshikovite (mnv: gray), which occurs at the contact of chalcopyrite and is associated with disseminated base-metal sulfides in the Oktyabr' deposit, Noril'sk complex. This grain of menshikovite occurs in intergrowth with sperrylite (*i.e.*, stoichiometric $Pt_{1.00}As_{2.00}$) and contains abundant micro-inclusions of an Ag-Au alloy $(Ag_{60.8\text{-}61.1}Au_{38.9\text{-}39.2})$ and paolovite enriched in As $[Pd_{2.05}(Sn_{0.60}As_{0.32}Sb_{0.03})_{\Sigma 0.95}$: EDS electron-microprobe data]. Scale bar (vertical) is 10 μm. A, B, and D: Back-scattered electron images. C: Reflected-light microphotograph.

chalcopyrite, maucherite, cobaltite, silicate mineral(s), quartz, and the *PGM*: paolovite, isomertieite, sperrylite, and hollingworthite (*e.g.*, Figs. 3A-C). Nine of these grains are single, and these may be subhedral (Fig. 3D). Menshikovite commonly occupies the central area of the polymineralic intergrowths (*e.g.*, Fig. 3A). It is sur-

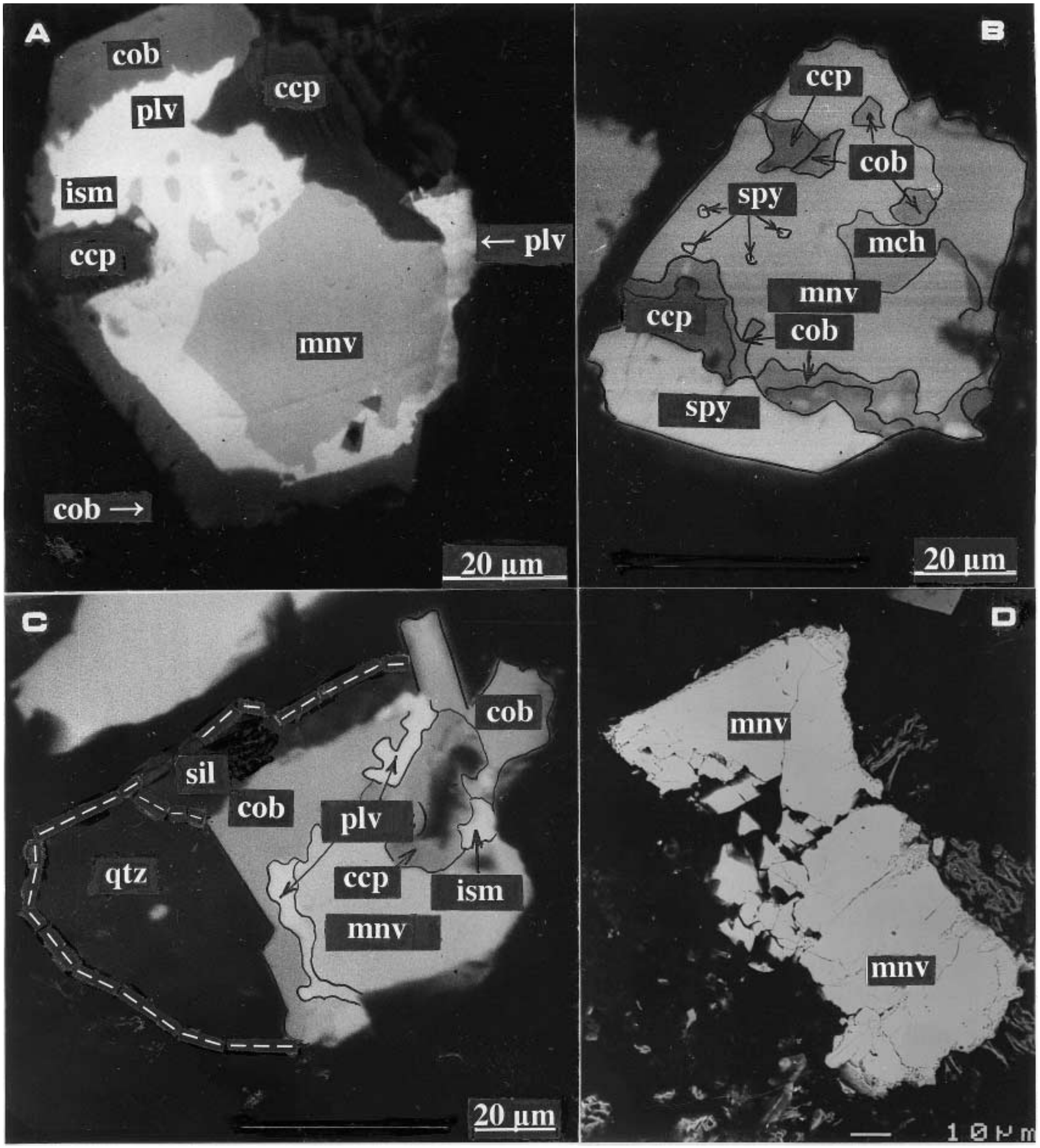

FIG. 3. Textural relationships of menshikovite from the Chiney complex. A. A skeletal crystal of cobaltite [cob: $(Co_{0.72}Ni_{0.23}Fe_{0.03})_{\Sigma 0.98}As_{1.02}S_{1.01}$)] contains menshikovite (mnv), paolovite (plv) and isomertieite (ism), which partly replace this menshikovite; note minute relics of menshikovite within the paolovite and isomertieite. ccp is chalcopyrite. B. A complex intergrowth of menshikovite (mnv) with maucherite (mch), sperrylite (spy), cobaltite (cob) and chalcopyrite (ccp). C. An intergrowth of menshikovite (mnv), paolovite (plv), isomertieite (ism), cobaltite (cob), and chalcopyrite (ccp) with quartz (qtz) and a Fe-rich aluminosilicate (sil). D. A large subhedral crystal of menshikovite (mnv). A-D: back-scattered electron images. The black material (Figs. A-D) is epoxy.

rounded (and is replaced) by paolovite and isomertieite, which may contain tiny relics of menshikovite, and these *PGM* are enclosed by a subhedral crystal of cobaltite (Fig. 3A).

Optical Properties and Microhardness

In reflected light at a high magnification, menshikovite is pink; a slight grayish tint may be observed. No bireflectance is observed in air. The anisotropy is weak, from light gray to brownish gray. A peculiar pattern of anisotropy, which is mosaic-like and probably reflects the presence of fine twins, is quite commonly observed. No cleavage or internal reflections were observed. The reflectance values for menshikovite from Lukkulaisvaara and Chiney are listed in Table 2. Though menshikovite from Lukkulaisvaara has a slightly higher reflectance, the reflectance spectra of menshikovite from these two localities are uniform and reveal about the same extent of bireflectance (Fig. 4).

Menshikovite is relatively hard, as indicated by our measurements of microhardness of menshikovite from Lukkulaisvaara. The observed ranges of microhardness values are VHN_{40} = 525.6 and 554.1, mean of 539.9 kg/mm^2 (two indentations: Carl Zeiss Neophot-2 tester), VHN_{50} = 500.5 – 569.0, mean of 534.7 kg/mm^2 (three indentations: PMT-3 tester), and VHN_{65} = 464.2 – 488.9, mean of 476.6 kg/mm^2 (two indentations: Carl Zeiss Neophot-2 tester). The average of these values is 517.1 kg/mm^2, close to the microhardness value VHN_{50} of majakite (520 kg/mm^2: Genkin *et al.* 1976), and corresponds to a Mohs hardness of ~5. It is noteworthy that if a load larger than VHN_{40-50} was used, fractured indentations commonly appeared. Menshikovite thus appears to be quite brittle.

TABLE 2. REFLECTANCE DATA FOR MENSHIKOVITE

	Lukkulaisvaara		Chiney		Lukkulaisvaara	
λ	R_1 air[§]	R_2 air[§]	R_1 air[§]	R_2 air[§]	R_1 oil*	R_2 oil*
400 nm	45.3%	47.1%	44.3%	47.4%	33.7%	34.0%
420	46.2	48.2	45.0	47.5	34.1	34.8
440	46.7	49.0	45.8	47.8	35.2	35.9
460	47.8	49.8	n.m.	n.m.	36.9	38.1
470	48.4	50.2	46.4	48.3	38.5	39.3
480	48.9	50.7	n.m.	n.m.	40.0	40.5
500	49.8	51.8	46.9	49.0	40.0	40.7
520	50.2	52.4	47.4	49.2	40.1	40.9
540	51.0	53.0	n.m.	n.m.	40.8	41.5
546	51.2	53.2	48.1	49.8	41.0	41.8
560	51.6	53.8	n.m.	n.m.	41.4	42.5
580	52.6	54.8	48.7	50.8	41.7	42.9
589	53.2	55.3	48.9	51.0	42.3	43.3
600	53.9	56.0	n.m.	n.m.	43.1	43.8
620	55.0	57.1	50.4	52.2	45.5	46.7
640	56.2	58.3	n.m.	n.m.	46.1	47.3
650	56.6	58.7	51.5	54.0	46.6	47.8
660	56.9	59.0	n.m.	n.m.	47.1	48.3
680	57.2	59.4	53.8	56.2	48.0	48.9
700	57.4	59.7	54.5	56.4	48.6	49.4

§ Reflectance values obtained with an MSFP-2 spectrophotometer.
* Reflectance values obtained with a Zeiss MPM spectrophotometer.
n.m.: not measured. The standard wavelengths (COM) are underlined.

Composition and Formula

Palladium, Ni and As are the main constituents of menshikovite in both of the occurrences at Lukkulaisvaara and Chiney. Concentrations of Pt, Cu, Sb, Te and S in the analyzed grains are lower than (or close to) the minimum detection-limits of the electron microprobe used (WDS). Cobalt is present only at a trace level in menshikovite from Chiney; in contrast, menshikovite from Lukkulaisvaara is totally devoid of Co.

Menshikovite from the Lukkulaisvaara intrusion

Menshikovite from Lukkulaisvaara has a quite constant composition (Table 3). The analytical data obtained on five grains of menshikovite from Lukkulaisvaara are internally consistent, agree with the ideal formula $Pd_3Ni_2As_3$, and are in agreement with results of analyses of a synthetic analogue of menshikovite (Barkov *et al.* 2000). A $\sum Me$: As ratio (atom proportions) of 1.67 is required by this ideal formula.

Menshikovite from the Chiney intrusion

In contrast, menshikovite from Chiney displays a notable compositional variation (Table 4). A strong negative correlation exists between the contents of Pd and As (correlation coefficient R = –0.93) in the compositions of menshikovite from Chiney (Fig. 5A). On the other hand, the concentration of Ni is nearly invariable in these compositions (Fig. 5B). The Pd–Ni correlation is negative and weak: R = –0.50 (Fig. 5C). The composition poor in Pd is closest to being stoichiometric in the series observed at Chiney (Table 4, Fig. 5A), and it leads to the empirical formula $[Pd_{3.00}(Ni_{1.98}Co_{0.01})_{\Sigma 1.99}As_{2.99}]$ which is close to the ideal formula $Pd_3Ni_2As_3$. An increase in the content of Pd accompanies the corresponding decrease in As (Fig. 5A), so that the composition richest in Pd is poor in As; it leads to the empirical formula $Pd_{3.15}(Ni_{1.97}Co_{0.01})_{\Sigma 1.98}As_{2.86}$, which displays a slight excess in Pd and a deficit in As relative to the ideal formula.

Menshikovite from the Oktyabr' deposit, Noril'sk complex

In a specimen from the Oktyabr' ore deposit, we have found a tiny grain of a Pd–Ni arsenide (Fig. 2D), whose composition is very close to that of menshikovite (Table 3). This grain is associated with disseminated base-metal sulfides, an Ag–Au alloy and *PGM*. Owing to the small grain-size and its close intergrowth rela-

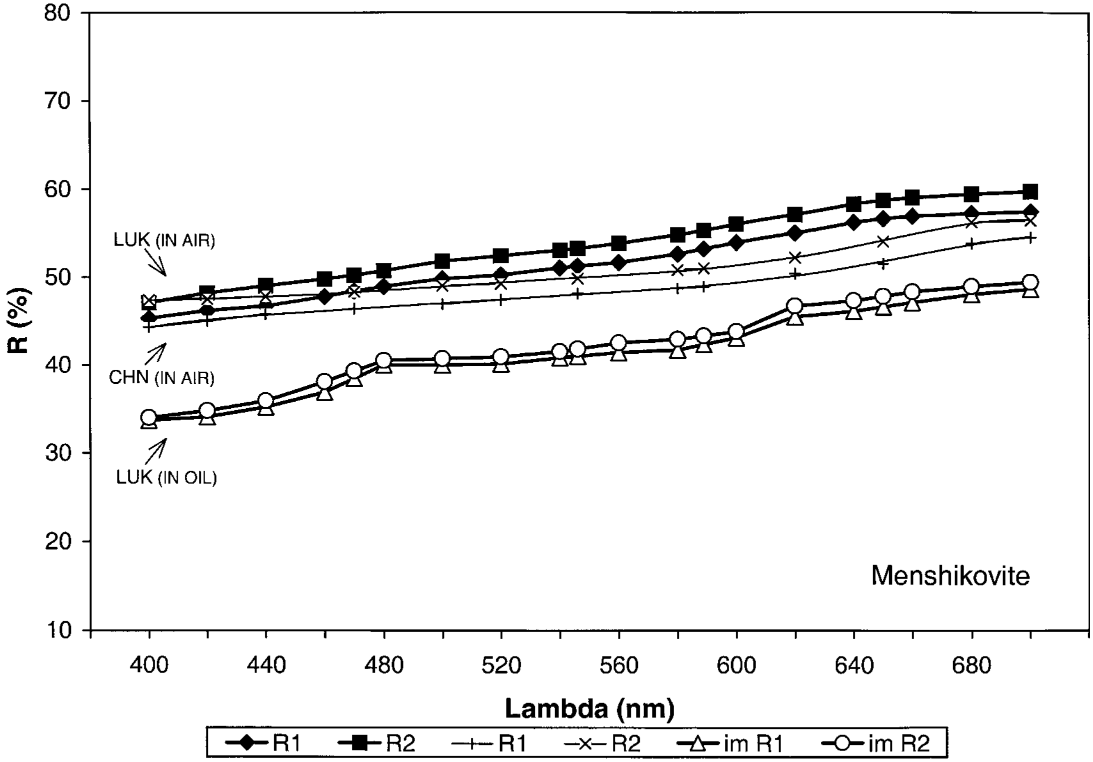

FIG. 4. Reflectance spectra for menshikovite from Lukkulaisvaara (LUK: bold lines) and Chiney (CHN), measured in air and in oil. The reflectance values (R %) are plotted *versus* wavelength λ in nm.

tionship with the associated minerals (Fig. 2D), no X-ray diffraction data could be obtained. The composition is consistent with the $Pd_3Ni_2As_3$ formula, and thus suggests that this Pd–Ni arsenide is menshikovite. Interestingly, this menshikovite also occurs in a close association with paolovite enriched in As (Fig. 2D), in common with menshikovite from Lukkulaisvaara and Chiney (Table 1).

X-RAY POWDER-DIFFRACTION DATA

An attempted study by a precession single-crystal method revealed the finely twinned nature of menshikovite (A.C. Roberts, writt. commun.). Single-crystal X-ray data thus could not be obtained, and the mineral was characterized by X-ray powder diffraction instead. The patterns obtained for menshikovite from Lukkulaisvaara and Chiney are in good agreement with each other. They both display significant differences from X-ray powder patterns of majakite (both natural and synthetic: Genkin *et al.* 1976), and rather suggest the existence of a structural relationship between menshikovite and synthetic Yb_5As_3. Synthetic Yb_5As_3 is hexagonal and has the Mn_5Si_3-type structure ($D8_8$), with the following unit-cell parameters: *a* 8.445-8.480 Å, *c* 6.618-6.671 Å, and Z = 2 (Ono *et al.* 1970). The $D8_8$ type of structure is characteristic of many various R_5X_3 compounds; it is known that this structure is flexible and can accommodate a very wide range of size differences of various participating atoms. On the basis of the general similarity of the X-ray powder patterns of menshikovite and synthetic Yb_5As_3 (Table 5), the pattern of menshikovite from Lukkulaisvaara was indexed with a hexagonal cell having the following parameters: *a* 8.406(4), *c* 6.740(4) Å, and *V* 412.4(6) $Å^3$. The powder pattern of menshikovite from Chiney, which is somewhat less complete (Table 5), could be indexed with similar parameters: *a* 8.416(12) and *c* 6.738(16) Å. The space groups $P6_3/m$, $P6_3$ and $P6_322$ are consistent with the X-ray powder data obtained for menshikovite.

Because of the small grain-size, the density of menshikovite could not be measured directly. For Z = 2, the calculated density is 5.32 g/cm^3. This value is quite low, when it is compared with densities of most *PGM*. Nevertheless, even such a low value would not be impossible, because the *PGM* are not necessarily dense, and the density of synthetic laurite (RuS_2) also is relatively low: 6.2 g/cm^3 (Cabri 1981). For Z = 4, the calculated density of menshikovite is 10.65 g/cm^3, and this value compares well with that of most of other *PGM*.

As in case of other finely twinned microminerals which have not yet been characterized in detail, a single-crystal X-ray study of synthetic or natural menshikovite is needed to confirm its crystallographic parameters proposed on the basis of the X-ray powder-diffraction data.

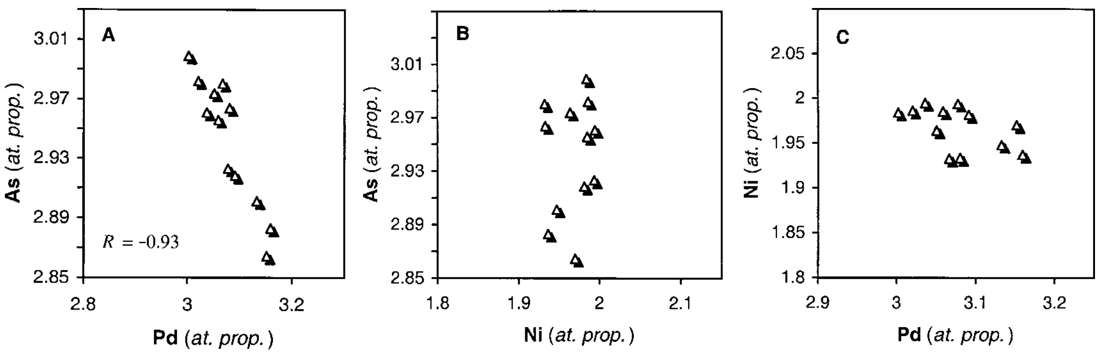

FIG. 5. Compositional variation of menshikovite from the Chiney complex. Concentrations of Pd *versus* As (A), Ni *versus* As (B), and Pd *versus* Ni (C) (atomic proportions, *at. prop.* based on Σ atoms = 8).

TABLE 3. AVERAGE RESULTS OF ELECTRON-MICROPROBE ANALYSES OF MENSHIKOVITE

	Lukkulaisvaara		Chiney		Noril'sk	Ideal formula
	1	2	3	4	5	6
n	78	20	12	1	5	
Pd wt.%	47.87	48.48	49.30	48.91	48.94	48.27
Pt	0.14	n.d.	n.d.	n.d.	n.d.	-
Ni	18.31	17.22	17.38	17.42	17.48	17.75
Co	n.d.	n.d.	0.12	0.13	n.d.	-
Fe	0.14	n.d.	n.d.	n.d.	n.d.	-
As	34.11	33.71	33.16	34.30	33.87	33.98
Total	100.57	99.41	99.96	100.76	100.29	100.00
Pd *apfu*	2.95	3.04	3.08	3.02	3.04	3.00
Pt	<0.01	-	-	-	-	-
Ni	2.05	1.96	1.97	1.95	1.97	2.00
Co	-	-	0.01	0.01	-	-
Fe	0.02	-	-	-	-	-
Σ*Me*	5.02	5.00	5.06	4.98	5.01	5.00
As	2.98	3.00	2.94	3.01	2.99	3.00

The results of wavelength-dispersion analyses (in weight %), which led to composition 1, were acquired with a JEOL–8900 instrument (20 kV, 30 nA). The X-ray lines and standards used were Pd$L\alpha$, Ni$K\alpha$ (metals) and As$K\alpha$ (synthetic InAs). Pt (detection limit: ≤0.1 wt.%), Cu, Sb and Te were sought, but not detected (n.d.). The analyses that led to compositions 2, 4 and 5 were carried out with a JEOL–733 instrument (15–20 kV, 15 nA). The X-ray lines and standards used were Pd$L\alpha$, Ni$K\alpha$ (metals) and As$K\alpha$ (InAs).
The analyses that led to composition 3 were made with a Camebax-Micro instrument (20 kV, 20–30 nA). The X-ray lines and standards used were Pd$L\alpha$, Ni$K\alpha$ (metals), and As$K\alpha$ (NiAs). The raw data were processed using a program of Lavrent'ev & Usova (1994).
The atomic proportions are based on eight atoms per formula unit (*apfu*). *n*: number of analyses made. Ideal formula: $Pd_3Ni_2As_3$.

TABLE 4. COMPOSITIONAL VARIATION§ OF MENSHIKOVITE FROM THE CHINEY LAYERED INTRUSION, RUSSIA

No.	Pd	Ni	Co	As	Sb	Total
1	49.37	17.45	0.08	32.81	n.d.	99.71
2	50.22	17.31	0.12	32.13	n.d.	99.78
3	49.25	16.65	0.18	31.57	0.11	97.76
4	49.22	17.47	0.10	33.77	n.d.	100.56
5	49.21	17.10	0.18	33.62	0.07	100.18
6	49.47	17.12	0.20	33.38	0.20	100.37
7	49.52	17.69	0.05	33.11	n.d.	100.37
8	50.93	17.46	0.16	33.20	n.d.	101.75
9	47.61	17.35	0.13	33.43	0.08	98.60
10	48.65	17.64	0.10	33.81	n.d.	100.20
11	48.90	17.71	0.07	33.56	n.d.	100.24
12	49.24	17.62	n.d.	33.49	n.d.	100.35
	Atomic proportions (Σ atoms = 8)					
	Pd	Ni	Co	Σ*Me*	As	Sb
1	3.09	1.98	0.01	5.08	2.92	-
2	3.15	1.97	0.01	5.14	2.86	-
3	3.16	1.94	0.02	5.12	2.88	<0.01
4	3.05	1.96	0.01	5.03	2.97	-
5	3.07	1.93	0.02	5.02	2.98	<0.01
6	3.08	1.93	0.02	5.04	2.95	0.01
7	3.08	1.99	<0.01	5.08	2.92	-
8	3.13	1.95	0.02	5.10	2.90	-
9	3.00	1.98	0.01	5.00	2.99	<0.01
10	3.02	1.99	0.01	5.02	2.98	-
11	3.04	1.99	<0.01	5.04	2.96	-
12	3.06	1.99	-	5.04	2.96	-

§ The results of wavelength-dispersion analyses (in weight %) were obtained with a Camebax-Micro instrument: see Table 3 for analytical details. n.d.: not detected.

The Relationship with Known Species and Phases, and a Solid Solution Involving Menshikovite

In spite of the existing similarity between the optical properties and microhardness values of menshikovite and majakite (ideally PdNiAs), these two minerals are clearly distinct in terms of their X-ray powder-diffraction data. For example, the strongest line in the pattern of menshikovite from Lukkulaisvaara, at 2.477 Å (I = 10), is also one of the strongest lines in the pattern of menshikovite from Chiney (2.49 Å, I = 6). In contrast, there is no such line in the patterns of majakite and its synthetic equivalent, which were characterized by Genkin *et al.* (1976). These authors suggested that majakite has the Fe_2P-type structure. Recently, a structural refinement has been done for synthetic PdNiAs, the analogue of majakite, on the basis of the β-Pd_2As structure of the Fe_2P type (Evstigneeva *et al.* 2000). Majakite thus appears to be related structurally with synthetic PdMnAs, which also has the Fe_2P-type structure (*e.g.*, Harada *et al.* 1990).

TABLE 5. X-RAY POWDER-DIFFRACTION DATA FOR MENSHIKOVITE

Menshikovite from Lukkulaisvaara§				Menshikovite from Chiney*				Synthetic Yb_5As_3 (Ono *et al.* 1970)			
I	*d* (Å) meas.	*d* (Å) calc.	*hkl*	I	*d* (Å) meas.	*d* (Å) calc.	*hkl*	I	*d* (Å) meas.	*d* (Å) calc.	*hkl*
4	4.20	4.203	110					4	4.244	4.240	110
3	3.65	3.640	200					21	3.675	3.672	200
								22	3.583	3.578	111
1	3.34	3.370	002					15	3.346	3.336	002
3	3.05	3.058	102	1	3.02	3.06	102	32	3.044	3.037	102
3	2.77	2.752	210	4	2.79	2.75	210	38	2.774	2.776	210
10	2.626	2.629	112	5	2.62	2.63	112	83	2.625	2.622	112
1	2.564	2.547	211					100	2.562	2.563	211
10	2.477	2.473	202	6	2.49	2.47	202	<4	2.471	2.467	202
8	2.429	2.427	300	6	2.43	2.43	300	59	2.447	2.448	300
				1	2.38						
7	2.283	2.283	301	9	2.27	2.29	301				
6	2.150	2.147	103	5	2.15	2.15	103				
6	2.105	2.102	220	3	2.11	2.10	220	<4	2.119	2.120	220
				1	2.04	2.02	310	<4	2.036	2.037	310
								<4	2.019	2.020	221
7	1.978	1.981	113	5	1.980	1.982	113	<4	1.971	1.969	113
3	1.936	1.934	311	1	1.938	1.936	311	4	1.947	1.948	311
3	1.912	1.912	203	4	1.910	1.912	203				
				1	1.863						
7	1.818	1.820	400	10	1.801	1.822	400	<4	1.835	1.836	400
7	1.781	1.783	222					25	1.790	1.789	222
6	1.757	1.757	401	8	1.749	1.741	213	33	1.738	1.738	312
				1	1.715					1.736	213
1	1.676	1.670	320	5	1.686	1.685	004	<4	1.684	1.685	320
				1	1.566	1.564	114	8	1.672	1.668	004
				1	1.545	1.548	411	19	1.633	1.634	321
								29	1.609	1.608	402
								29	1.602	1.603	410
2	1.492	1.496	322	4	1.493	1.498	322				
1	1.424	1.423	501	4	1.422	1.425	501				
2	1.372	1.372	331	2	1.398	1.403	330				
				2	1.358	1.350	421				
3	1.341	1.340	323	4	1.341	1.341	323				
2	1.312	1.315	224	2	1.279	1.275	422				
2	1.280	1.284	115,511	2	1.271	1.264	205				
5	1.237	1.236	404	6	1.238	1.237	404				
				1	1.216	1.215	600				
1	1.164	1.166	520								
1	1.153	1.156	414	1	1.158	1.157	414				
2	1.144	1.142	602	2	1.140	1.143	602				
1	1.069	1.073	206								
		1.068	603								
1	1.050	1.051	440								
		1.049	325								
3	1.030	1.033	514								
		1.028	701,531								

§ Pattern obtained with a 114.6 mm Debye-Scherrer camera, Fe$K\alpha$ radiation.
* Pattern obtained with a 57.3 mm Gandolfi camera, Fe$K\alpha$ radiation. The intensities were estimated visually.

The compositions of menshikovite from Lukkulaisvaara and of the relatively Pd-poor menshikovite from Chiney are consistent with the atomic $\sum Me$: As ratio of 5 : 3 (Tables 3, 4, Figs. 5A, B). These compositions are similar to that of the synthetic analogue of menshikovite (Gervilla *et al.* 1994, Barkov *et al.* 2000). Similar atomic proportions also are characteristic of Pd–Ni arsenides reported from the Stillwater complex (Cabri *et al.* 1975), Two Duck Lake intrusion, Coldwell complex, Ontario (Mulja & Mitchell 1990), Monchegorsk layered complex, Kola Peninsula, Russia (Grokhovskaya *et al.* 2000), and from the Oktyabr' deposit, Noril'sk complex (Table 3: this study).

Majakite has a $\sum Me$: As ratio close to 2 (Genkin *et al.* 1976, 1981, Vuorelainen *et al.* 1982). A Ni-for-Pd substitution likely exists in majakite, as is implied by the composition $Pd_{0.92}Ni_{1.10}As_{0.98}$ reported by Genkin *et al.* (1976). Majakite associated with menshikovite at Chiney has the composition $Pd_{0.99}Ni_{1.02}(As_{0.97}Sb_{0.01})_{\Sigma 0.98}$ (this study), *i.e.*, its $\sum Me$: As ratio also is close to 2. Chen *et al.* (1993) reported a Pd–Ni arsenide, which likely is related to majakite, from the Thompson mine, Manitoba. No X-ray powder data were reported for this phase, which has the composition $Pd_{1.13}Ni_{0.82}As_{1.04}$; the $\sum Me$: As ratio is 1.88.

In Figures 6 to 9, we have summarized the available compositional data on menshikovite and the natural phases similar to menshikovite in composition (open symbols) and on majakite and the related phase from the Thompson mine (filled squares). The compositional trends of majakite suggest the existence of a positive correlation between Pd and As (Fig. 6), a negative Ni–As correlation (Fig. 7), and a negative Ni–Pd correlation (Fig. 8).

A solid-solution series seems to exist between majakite and menshikovite (Fig. 9). The total content of metals decreases, and the content of As increases toward menshikovite in this series (Fig. 9). Compositions of the menshikovite series from Chiney vary from $Pd_{3.00}(Ni_{1.98}Co_{0.01})_{\Sigma 1.99}As_{2.99}$ to $Pd_{3.15}(Ni_{1.97}Co_{0.01})_{\Sigma 1.98}As_{2.86}$, and display a strong negative Pd–As correlation; Ni varies slightly in this series and does not correlate with As (Figs. 5A–C). One reviewer of the present manuscript has proposed that "the negative correlation between Pd and As could be due to As loss during interaction with fluids". This proposal is not consistent with the following observations, however: (1) No signs of alteration were observed in all of the analyzed grains of menshikovite from the Chiney complex. (2) We are not aware of the existence of any experimental data, which would have shown that such loss of As could occur in a Pd–Ni arsenide. (3) Compositions of menshikovite at Chiney clearly display the same trend as the other related Pd–Ni arsenides reported in the literature. On the (Pd + Ni) – As diagram (Fig. 9), all of these compositions plot on the line between menshikovite and majakite; this feature is notable and would hardly be expected in case of a selective removal of As by fluids. (4) In addition, there is no evidence of As loss in case of the other Pd–Ni arsenides reported in the literature (Cabri *et al.* 1975, Genkin *et al.* 1976, 1981, Vuorelainen *et al.* 1982, Mulja & Mitchell 1990, Chen *et al.* 1993). Our observations (Fig. 9) thus imply the existence of a series of solid solutions between menshikovite and majakite [*i.e.*, $(Pd,Ni)_2As$ of the β-Pd_2As type], and further studies involving an experimental investigation are required to better characterize this series.

Genetic Implications

The Lukkulaisvaara intrusion

Many similarities exist among the mineralized pods and stringers of the coarse-grained (locally pegmatitic) mafic rocks, altered to various extents. The pods that occur in the Nadezhda and Vostok *PGE* deposits, located in different areas of the Lukkulaisvaara intrusion, display the following similarities, among others: (1) The existence of a close association of (and a genetic relationship between) these pods and the host microgabbronorite. (2) A strong enrichment of the pods in base-metal sulfides (up to 30 vol.%), dominantly chalcopyrite. (3)

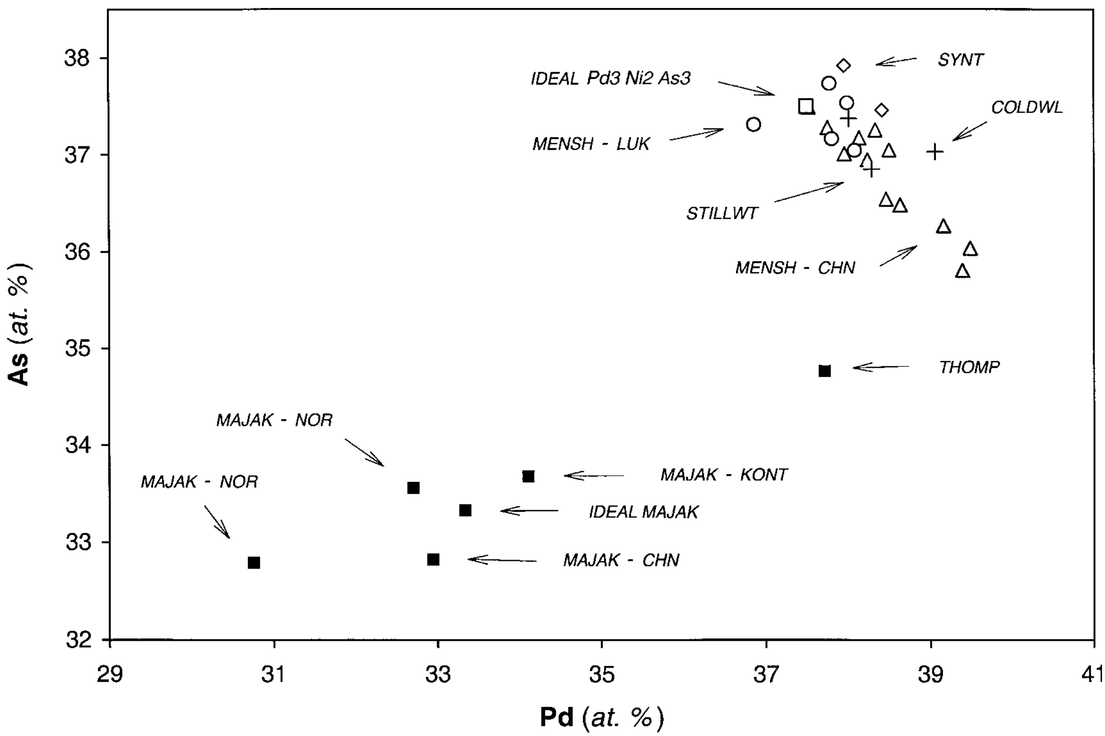

FIG. 6. Concentration of Pd *versus* As (at. %) for menshikovite and phases related to menshikovite (open symbols) and for majakite and phases related to majakite (filled symbol). *MENSH – LUK* (open circles): menshikovite from the Lukkulaisvaara intrusion (this study and Barkov *et al.* 2000). *SYNT* (open diamonds): synthetic menshikovite (Barkov *et al.* 2000). *MENSH – CHN* (open triangles): menshikovite from the Chiney intrusion (this study). *STILLWT* (cross): Pd-Ni arsenide, related to menshikovite, from the Stillwater complex (Cabri *et al.* 1975). *COLDWL* (cross): Pd-Ni arsenide, related to menshikovite, from the Coldwell complex (Mulja & Mitchell 1990). *OKTYABR* (cross): Pd-Ni arsenide, related to menshikovite, from the Oktyabr' deposit, Noril'sk (this study). *MAJAK-NOR* (filled square): majakite from the Noril'sk complex (Genkin *et al.* 1976, 1981). *MAJAK – KONT* (filled square): majakite from the Konttijärvi intrusion (Vuorelainen *et al.* 1982). *MAJAK – CHN* (filled square): majakite from the Chiney intrusion (this study). *THOMP* (filled square): Pd-Ni arsenide, related to majakite, from the Thompson mine (Chen *et al.* 1993).

The presence of whole-rock concentrations of the *PGE*, especially Pd. (4) An enrichment in Ag, and the presence of Ag-rich PGM and other Ag-rich minerals in association with the *PGM*. (5) The presence of Pd-, Pt- and Ag-rich tellurides, the main minerals of noble metals in these pods. (6) The occurrence of the unnamed Re-rich sulfide in these pods (Barkov & Lednev 1993).

These *PGE*-rich pods and stringers formed as a result of a local concentration of magmatic volatiles during crystallization of the host bodies of microgabbronorite (*e.g.*, Barkov *et al.* 2001). Chlorine was an abundant constituent of a hydrous fluid at a postmagmatic–hydrothermal stage of crystallization of the *PGE*-rich pods at the Nadezhda deposit. Ferropargasite and its unnamed Cl-dominant analogue, which are strongly enriched in Cl (up to 4.5 wt.%), occur there in a close textural association with *PGM* (Barkov *et al.* 2001). In contrast, no Cl-rich minerals were observed in the menshikovite-bearing pod at the Vostok deposit, and the actinolite and clinochlore are totally devoid of Cl in that deposit. On the other hand, the highly magnesian and K-, Fe-, Al-poor composition of the actinolite strongly suggests that crystallochemical constraints, rather than a Cl-depleted environment, are the likely reason for the Cl-free composition (*cf.* Oberti *et al.* 1993).

The association of menshikovite with hydrous silicates (*e.g.*, Figs. 2A,B) and the presence of the veinlet-like grain that transects a hydrous silicate (Fig. 2C), suggest a rather low temperature of formation for menshikovite in the Vostok deposit. The occurrence of menshikovite in the Oktyabr' deposit (Fig. 2C) is also consistent with a late-stage crystallization. Probably, menshikovite formed at a postmagmatic–hydrothermal stage of crystallization from microvolumes of a hydrous fluid or a residual liquid. This suggestion is quite consistent with the appearance of the synthetic analogue of menshikovite at a temperature as low as 450°C (Gervilla *et al.* 1994).

The Chiney intrusion

The Pd-rich mineralization, which occurs in the mineralized sandstones in the zone of exocontact, appears to have formed from a volatile-rich fluid, primarily derived from magma of the Chiney intrusion. The *PGE* were thus remobilized, transported and deposited from this fluid to form menshikovite and the *PGM* associated with menshikovite.

In the mineralized zone, menshikovite coexists with Pd-bearing maucherite (*e.g.*, Fig. 3B), which contains

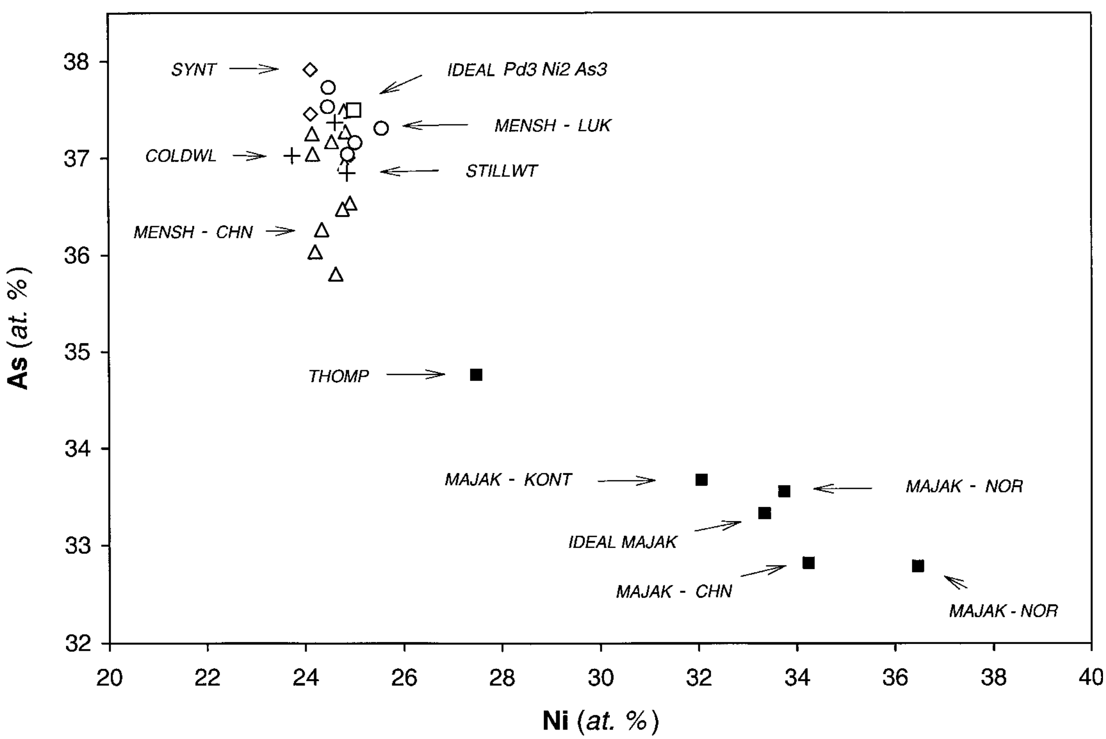

FIG. 7. Concentration of Ni *versus* As (at. %) for menshikovite and phases related to menshikovite (open symbols) and for majakite and phases related to majakite (filled symbol). The abbreviations are the same as in Figure 6.

up to 2.1 at.% Pd. According to the experimental results of Gervilla *et al.* (1994), the maximum solubility of Pd in maucherite is 1.5 at.% at 790°C, and increases with a decrease in temperature to reach 5.5 at.% Pd at 450°C. A strong enrichment in volatile species appears to have taken place in the environment existing at the zone of exocontact. Thus, the concentration of volatiles could cause a significant decrease in temperatures of crystallization of the Pd-bearing maucherite at Chiney, relative to the temperatures suggested by the experimental data.

Menshikovite occurs in a central area of the polymineralic intergrowth, and as minute relics within the other *PGM* (Fig. 3), and likely formed at an earlier stage of the crystallization. The cobaltite–gersdorffite, which is closely associated with menshikovite in these complex intergrowths, is strongly enriched in the cobaltite end-member [*e.g.*, $(Co_{0.72-0.75}Ni_{0.19-0.23}Fe_{0.03-0.04})_{\Sigma 0.98}As_{0.98-1.02}S_{1.01-1.04}$]. This cobaltite thus is similar to cobaltite that forms part of cryptically zoned crystals in the Mt. General'skaya layered intrusion, Kola Peninsula (Barkov *et al.* 1999b). According to the experimental data of Klemm (1965), the cobaltite at Chiney must have crystallized at low temperatures (≤500°C). The relatively low-temperature character of this cobaltite is in good agreement with its occurrence as skeletal crystals (Fig. 3A). Observations reported from the Mt. General'skaya also are consistent; there, crystals of (*PGE*-rich) cobaltite-gersdorffite become progressively enriched in the cobaltite end-member during crystallization, from the center to the edge, with the *PGE* substituting isomorphously for Co (Barkov *et al.* 1999b).

Acknowledgements

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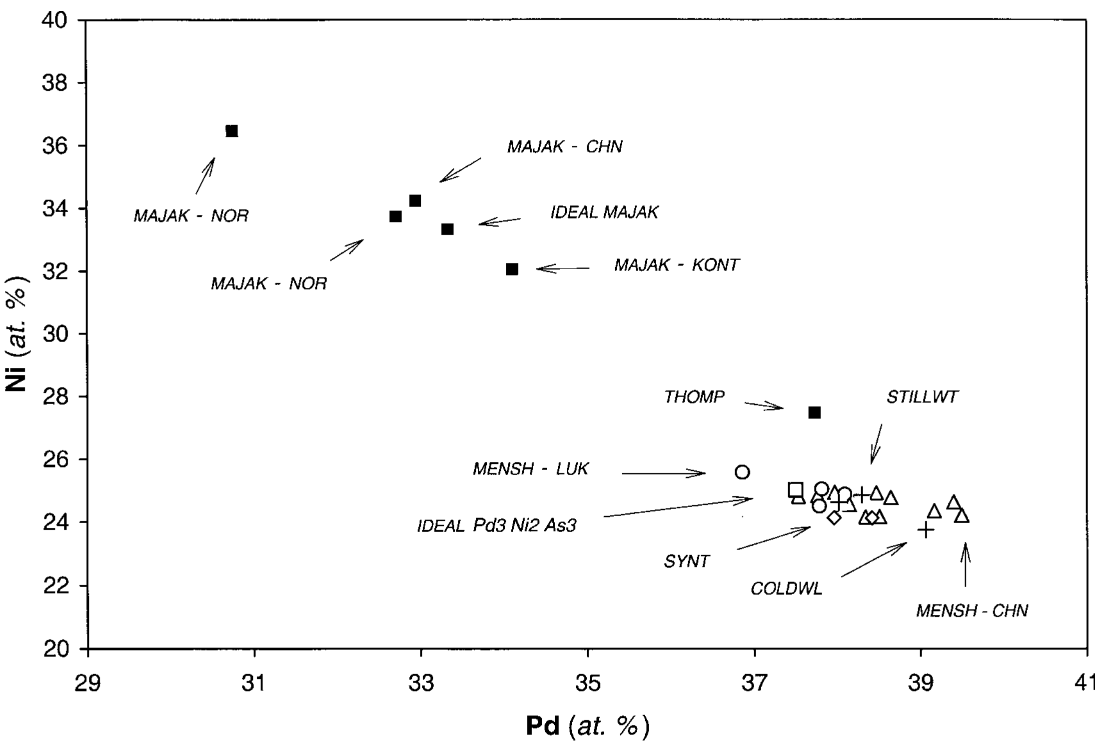

FIG. 8. Concentration of Pd *versus* Ni (at. %) for menshikovite and phases related to menshikovite (open symbols) and for majakite and phases related to majakite (filled symbol). The abbreviations are the same as in Figure 6.

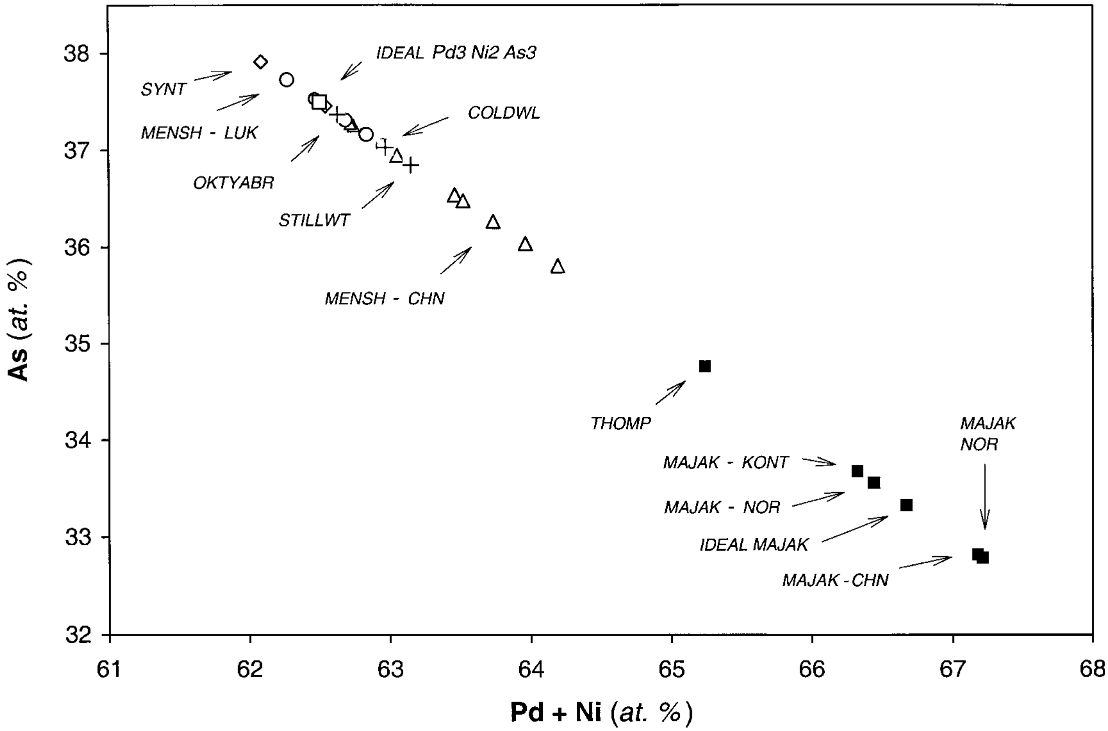

FIG. 9. Concentration of (Pd + Ni) *versus* As (at. %) for menshikovite and phases related to menshikovite (open symbols) and for majakite and phases related to majakite (filled symbol). Where present, minor concentrations of Pt, Co and Fe were added to (Pd + Ni), and minor concentrations of Te and Sb were added to As. The abbreviations are the same as in Figure 6.

pleased to submit the present manuscript for publication in the special issue devoted to Dr. Louis J. Cabri, who reported the first occurrence of a Pd–Ni arsenide, which is similar to menshikovite in composition, from the Stillwater complex. The manuscript was improved by helpful comments made by Dr. F. Gervilla, an anonymous referee and Associate Editor N.J. Cook.

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