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Menshikovite, Pd-Ni arsenide and synthetic equivalent

A. Y. Barkov[1,*], K. Laajoki[2], F. Gervilla[3] and E. Makovicky[4]

[1] Department of Earth and Planetary Sciences, McGill University, 3450 University Street, Montreal, Quebec H3A 2A7, Canada
[2] Department of Geology, University of Oulu, FIN-90570 Oulu, Finland
[3] Department of Mineralogy and Petrology, University of Granada, Avda. Fuentenueva, s/n, 18002 Granada, Spain
[4] Department of Mineralogy and Petrology, University of Copenhagen, Østervoldgade 10, 1350 Copenhagen, Denmark

ABSTRACT

The average compositions of menshikovite ($Pd_3Ni_2As_3$) from the type locality (Lukkulaisvaara layered intrusion, Russian Karelia) and a Pd-Ni arsenide synthesized at 450°C, are very close. The observed ΣMetal:As ratio is close to 5:3, as in the case of previously described arsenides from the Stillwater and Two-Duck Lake intrusions. The compositions suggest that these unnamed Pd-Ni arsenides and the synthetic phase are in fact menshikovite.

Keywords: menshikovite, Pd-Ni arsenide, platinum group mineral, Pd-Ni-As, Lukkulaisvaara, Russian Karelia.

Introduction

Menshikovite, $Pd_3Ni_2As_3$, is a new Pd-Ni arsenide from the Lukkulaisvaara (Russian Karelia) and Chiney (Siberia) mafic-ultramafic layered intrusions, Russia. Both the new mineral and its name have been approved by the CNMMN, IMA (Barkov *et al.*, in prep.). Previously, electron-microprobe data on Pd-Ni arsenides that are similar in composition to menshikovite were reported from the Stillwater (USA), Two-Duck Lake and Geordie Lake (Canada) intrusions (Cabri *et al.*, 1975; Mulja and Mitchell, 1990). Menshikovite and these unnamed phases differ in atomic proportions (and X-ray data) from majakite (or mayakite), ideally PdNiAs, initially discovered at Noril'sk (Genkin *et al.*, 1976; Genkin *et al.*, 1981), and subsequently described from the Konttijärvi layered intrusion in Finland (Vuorelainen *et al.*, 1982). Synthetic analogues of menshikovite and majakite were reported to exist in the system Pd-Ni-As at 450°C (Gervilla *et al.*, 1994).

* E-mail: barkov@eps.mcgill.ca

The present study was undertaken to compare the compositions of menshikovite and the related Pd-Ni arsenide, synthesized by Gervilla *et al.* (1994). In order to avoid additional analytical errors, representative natural and synthetic materials were analysed almost simultaneously, using the same analytical facilities. Menshikovite interlayers in the synthetic runs are relatively thin (this textural feature is due to sluggish reaction rates at the conditions of the synthesis at 450°C), and we thus preferred to obtain the bulk of analytical data by means of quantitative energy-dispersion spectrometry (EDS).

Samples

The menshikovite grains analysed are from the type locality, the Lukkulaisvaara layered intrusion (Vostok deposit) of the Russian Karelia. The mineral occurs in a coarse-grained, completely-altered gabbronorite located within a micro-gabbronorite. There are no relics of primary igneous minerals in this gabbronorite, and the rock is composed of actinolite and subordinate chlorite (clinochlore). The gabbronorite is rich in base-metal sulphides (up to 30 modal %; predominantly chalcopyrite and pentlandite).

Violarite is a common replacement product of the pentlandite. Associated platinum-group minerals (PGM) include merenskyite, members of the kotulskite-sobolevskite solid-solution series, michenerite, sopcheite, mertieite or stibiopalladinite, As-bearing paolovite and an unnamed $Pd_2(Sn_{0.5}Sb_{0.5})$. An unusually Os-rich hollingworthite and a cobaltite-gersdorffite rich in Rh (up to 9 wt.% Rh) are the Rh-rich minerals in the deposit (Barkov *et al.*, 1996). Hessite and argentopentlandite occur in spatial association with the PGM. Of particular interest is the presence of an unnamed rhenium-rich sulphide, $(Cu,Fe)(Re,Mo)_4S_8$ (Barkov and Lednev, 1993).

Menshikovite typically appears as anhedral, individual grains (up to 0.15 mm in the longest dimension), located within chalcopyrite and at the border between the latter and hydrous silicate (Fig. 1*a*). Rarely, menshikovite occurs as veinlet-like grains among the hydrous silicates. This texture implies a rather low temperature of formation for this Pd-Ni arsenide, consistent with the appearance of the synthetic menshikovite at 450°C in the system Pd-Ni-As (Gervilla *et al.*, 1994).

In the experimental charges analysed, the synthetic equivalent of menshikovite typically occurs as thin interlayers of 20–30 μm across. It is characteristically associated with Pd-bearing NiAs and $(Pd,Ni)_2As$ phases, which never occur in immediate contact with each other, but are invariably separated by thin bands of the synthetic menshikovite (e.g. Fig. 1*b*).

TABLE 1. Compositions of menshikovite, its synthetic equivalent and related natural arsenides.

	Menshikovite				Unnamed arsenide		Synthetic menshikovite			
No.	1	2	3	4	5	6	7	8	9	10
	n = 6	*n* = 16	*n* = 14	Average		*n* = 3	*n* = 8	*n* = 6	Average	*n* = 1
Pd	48.62	48.48	48.87	48.66	48.6	49.60	48.72	49.26	48.99	49.12
Pt	n.d.	n.d.	n.d.	n.d.	–	0.38	–	–	–	–
Ni	17.75	17.33	17.60	17.56	17.4	16.63	17.08	17.06	17.07	17.57
As	33.64	34.08	33.46	33.73	32.7	33.10	34.26	33.81	34.04	33.22
Te	n.d.	n.d.	n.d.	n.d.	0.38	–	–	–	–	–
Total	100.01	99.89	99.93	99.95	99.08	99.71	100.06	100.13	100.10	99.91
Atom.%										
Pd	37.81	37.78	38.09	37.89	38.29	39.06	37.96	38.42	38.18	38.33
Pt	–	–	–	–	–	0.16	–	–	–	–
Ni	25.03	24.49	24.87	24.80	24.86	23.75	24.13	24.13	24.13	24.86
ΣM	62.84	62.27	62.96	62.69	63.15	62.97	62.09	62.55	62.31	63.19
As	37.16	37.73	37.04	37.31	36.60	37.03	37.92	37.46	37.69	36.82
Te	–	–	–	–	0.25	–	–	–	–	–
Atomic proportions (Σ atoms = 8)										
Pd	3.03	3.02	3.05	3.03	3.06	3.13	3.04	3.07	3.05	3.07
Pt	–	–	–	–	–	0.01	–	–	–	–
Ni	2.00	1.96	1.99	1.98	1.99	1.90	1.93	1.93	1.93	1.99
ΣM	5.03	4.98	5.04	5.01	5.05	5.04	4.97	5.00	4.98	5.06
As	2.97	3.02	2.96	2.98	2.93	2.96	3.03	3.00	3.01	2.95
Te	–	–	–	–	0.02	–	–	–	–	–
ΣMet:As(+Te)										
	1.69	1.65	1.70	1.68	1.71	1.70	1.64	1.67	1.65	1.72

1- 3: menshikovite from the type locality (Lukkulaisvaara); 4: average of analyses 1–3 (this study).
5: unnamed arsenide from Stillwater (Cabri *et al.*, 1975).
6: unnamed arsenide from Two-Duck Lake (Mulja and Mitchell, 1990).
7 and 8: synthetic menshikovite; 9: average of analyses 7 and 8 (EDS analyses, this study).
10: synthetic menshikovite (WDS analysis, this study).
n = number of analyses; n.d. = not detected

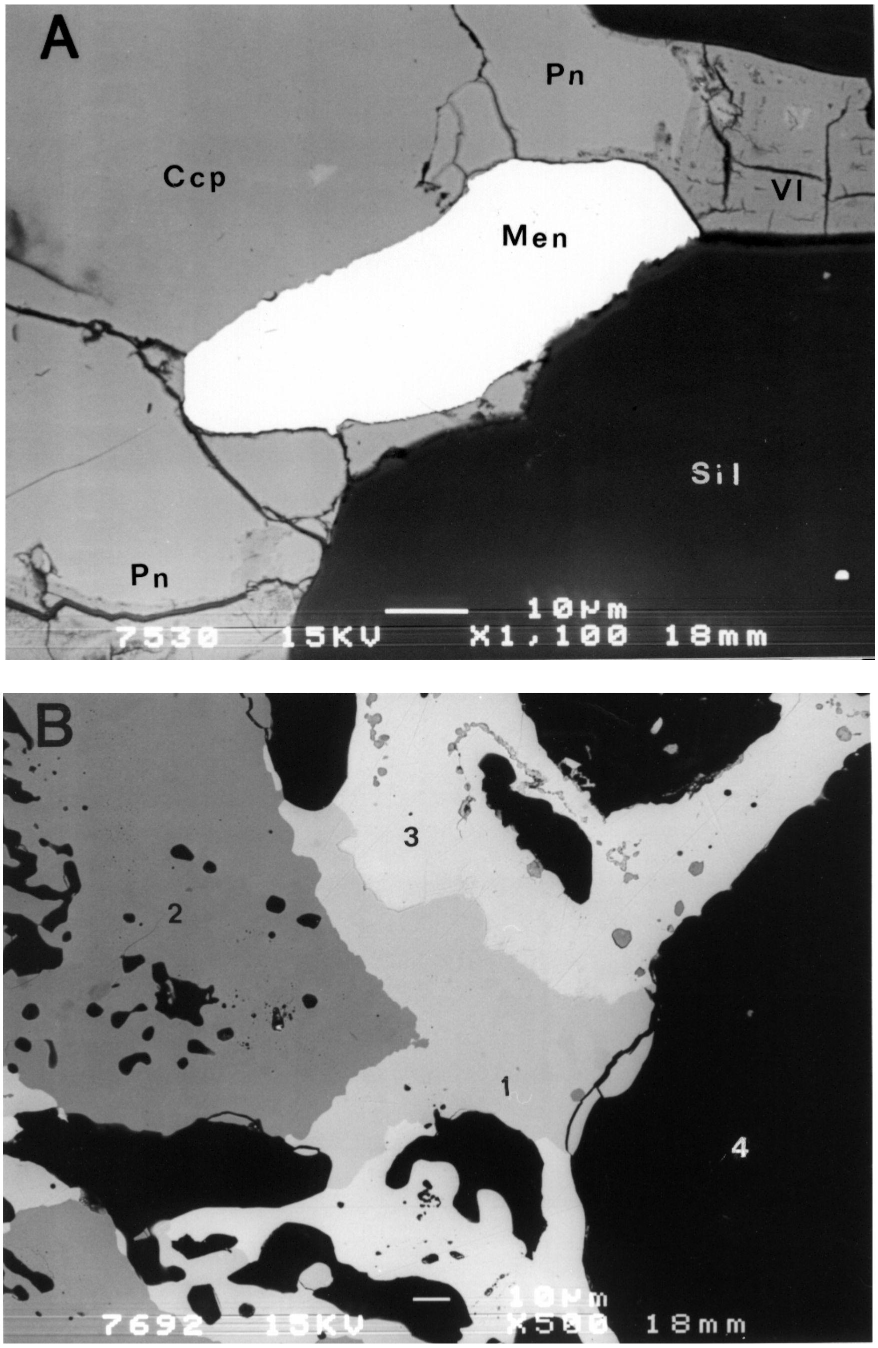

FIG. 1. Textural relationships of menshikovite from Lukkulaisvaara and its synthetic equivalent with associated minerals and phases. Back-scattered electron images; scale bars: 10 μm. (*a*) Menshikovite (Men) located at the border between chalcopyrite (Ccp) and hydrous silicate (Sil; probably actinolite). Pn: pentlandite, Vl: violarite. (*b*) Synthetic menshikovite (1), coexisting with the phases $(Ni_{0.91}Pd_{0.06})_{\Sigma 0.97}As_{1.03}$ (2) and $(Pd_{1.74}Ni_{0.25})_{\Sigma 1.99}As_{1.01}$ (3). 4 = epoxy (black). Charge No. 10.

Analytical methods

The EDS electron microprobe analyses of menshikovite and the related synthetic phase were carried out using a JEOL JSM-6400 scanning electron microscope, equipped with a LINK eXL energy dispersion spectrometer. The analytical conditions were: accelerating voltage of 15 kV and beam current of 1.2 nA, and the following analytical lines (and standards) were used: Pd-L (pure Pd and $Pd_{11}Sb_2As_2$), As-L ($PtAs_2$) and Ni-K (pure metal). The counting periods were 100 s. A finely focused beam ($\leqslant 1$ μm) was applied in all the analyses. The Link ISIS (version 3.00) and ZAF-4 (anal. 1, Table 1) programs were used to process the spectra on-line. The estimated errors in the EDS analyses for Pd, Ni and As are $\leqslant 0.4$, $\leqslant 0.3$ and $\leqslant 0.2$ wt.%, respectively.

A wavelength-dispersion (WDS) electron microprobe analysis of the synthetic menshikovite was carried out using a JEOL-733 microprobe, at 15 kV and 15 nA. The $L\alpha$ line was used for Pd and $K\alpha$ line for Ni and As. The standards used were synthetic InAs and pure metals.

Results

Fifty EDS analyses of the Lukkulaisvaara menshikovite (36 analyses) and its synthetic analogue (14 analyses) gave analysis totals in the range of 99.1 to 100.75 wt.% (mostly between 99.4 and 100.5 wt.%). The average results are presented in Table 1, in comparison with compositions of related natural phases from the literature. The average compositions of the menshikovite and related synthetic phase are very close to each other. The ΣMetal:As ratio (atom.%) of the menshikovite varies from 1.65 to 1.70 and for the synthetic analogue from 1.64 to 1.72. The average composition of the natural and synthetic menshikovite (Table 1) is consistent with the formula $Pd_3Ni_2As_3$ (ΣMetal:As = 1.67).

The compositions of menshikovite and its synthetic analogue are similar to those of the natural Pd-Ni arsenides from the Stillwater and Two-Duck Lake intrusions (ΣMetal:As = 1.70 - 1.71) (Cabri *et al.*, 1975; Mulja and Mitchell, 1990). The other Pd-Ni arsenide, majakite, differs in atomic proportions and has a ΣMetal:As ratio of close to 2 (Genkin *et al.*, 1981; Vuorelainen *et al.*, 1982). The synthetic majakite also gives the ΣMetal:As ratio close to 2 (i.e. 1.94–1.99; Gervilla *et al.*, 1994). Chen *et al.* (1993) reported a majakite-like phase from the Thompson mine, Canada, which has a lower ΣMetal:As ratio of 1.88. This phase has a composition intermediate between that of majakite and $(Pd,Ni)_{2-x}As$, and may represent a low-temperature extension of the $(Pd,Ni)_{2-x}As$ solid solution (Gervilla *et al.*, 1994).

In conclusion, the compositions (Table 1) suggest that previously-described, unnamed Pd-Ni arsenides and the synthetic phase are in fact menshikovite.

Acknowledgements

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