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COMPOSITIONAL VARIATIONS IN OULANKAITE AND A NEW SERIES OF ARGENTOAN OULANKAITE FROM THE LUKKULAISVAARA LAYERED INTRUSION, NORTHERN RUSSIAN KARELIA

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ABSTRACT

Oulankaite, a complex base- and precious-metal stannosulfotelluride from the Nadezhda deposit in the Lukkulaisvaara layered intrusion, northern Karelia, northwestern Russia, exhibits a considerable variation in composition. At the type locality, this unique species of platinum-group mineral (PGM) is associated with various base-metal sulfides and PGM in hydrothermally altered pods and stringers of coarse-grained to pegmatitic gabbronorite, located within a sill-like body of microgabbronorite. Covariations in contents of (Pd + Pt) and (Cu + Fe + Ag) are observed in Ag-poor oulankaite (<0.1 wt.% Ag) and in a new compositional series of argentoan oulankaite (up to 1.52 Ag atoms per formula unit, *apfu*: Σatoms = 14). On the basis of the new data, we suggest a revised generalized formula for oulankaite: $(Pd,Pt)_{5+x}(Cu,Fe,Ag)_{4-x}SnTe_2S_2$, with $0 \le x < 1$. The formula of the Ag-dominant analogue of oulankaite is similar: $(Pd,Pt)_{5+x}(Ag,Cu,Fe)_{4-x}SnTe_2S_2$, with $0 \le x < 1$. Two different mechanisms of substitution exist in argentoan oulankaite, Ag-for-Cu and Pd-for-(Cu+Ag), whereas the composition of Ag-poor oulankaite is dominated by Pd-for-Cu substitution. Argentoan oulankaite ranges up to $(Pd_{5.31}Pt_{0.17})_{\Sigma5.48}(Ag_{1.52}Cu_{1.27}Fe_{0.63})_{\Sigma3.42}Sn_{1.03}Te_{2.09}S_{1.98}$, which is likely an unnamed species of PGM. Micro-inclusions of Cl-rich ferropargasite (up to 3.25 wt.% Cl) occur in argentoan oulankaite and Ag-poor oulankaite. The argentoan oulankaite solid-solution probably formed from microvolumes of a late-stage liquid or fluid rich in Pd, Ag, Cu, Sn, Te, and S, which is consistent with the Pd–(Pt)–Ag mineralization in the Nadezhda deposit.

Keywords: oulankaite, solid solution, sulfotelluride, platinum-group elements, platinum-group minerals, layered intrusion, Lukkulaisvaara, Russian Karelia, Baltic Shield.

SOMMAIRE

L'oulankaïte, stannosulfotellurure complexe de métaux de base et de métaux précieux provenant du gisement de Nadezhda, complexe stratiforme de Lukkulaisvaara, dans le nord de la Karélie, secteur nord-ouest de la Russie, fait preuve d'une variation importante en composition. À la localité type, cette espèce unique parmi les minéraux du groupe du platine (MGP) est associée à plusieurs sulfures de métaux de base et de MGP dans des lentilles de gabbronorite à grains grossiers, voire pegmatitiques, montrant les effets d'une altération hydrothermale, le tout à l'intérieur d'un filon-couche de microgabbronorite. Nos documentons des covariations en teneurs de (Pd + Pt) et de (Cu + Fe + Ag) dans l'oulankaïte à faible teneur en Ag (<0.1%, poids) et une nouvelle solution solide d'oulankaïte argentifère (jusqu'à 1.52 atomes de Ag par formule unitaire, *apfu*: Σatomes = 14). À la lumière des données nouvelles, nous proposons une formule révisée pour décrire le pôle à faible teneur en Ag: $(Pd,Pt)_{5+x}(Cu,Fe,Ag)_{4-x}SnTe_2S_2$, avec $0 \le x < 1$. La formule de l'analogue à dominance d'argent est semblable: $(Pd,Pt)_{5+x}(Ag,Cu,Fe)_{4-x}SnTe_2S_2$, avec $0 \le x < 1$. Deux mécanismes différents existent dans l'oulankaïte argentifère, Ag-pour-Cu et Pd-pour-(Cu+Ag), tandis que la composition de l'oulankaïte dépourvue d'argent répond à la seule substitution Pd-pour-Cu. L'oulankaïte argentifère atteint la composition $(Pd_{5.31}Pt_{0.17})_{\Sigma5.48}(Ag_{1.52}Cu_{1.27}Fe_{0.63})_{\Sigma3.42}Sn_{1.03}Te_{2.09}S_{1.98}$, qui serait probablement une nouvelle espèce de MGP. Des micro-inclusions de ferropargasite riche en chlore (jusqu'à 3.25% Cl, poids) sont présentes dans les deux espèces. Les membres de la nouvelle solution solide se seraient formés à partir de microvolumes d'un liquide ou fluide tardif enrichi en Pd, Ag, Cu, Sn, Te, et S, ce qui est conforme à la minéralisation en Pd–(Pt)–Ag au gisement de Nadezhda.

(Traduit par la Rédaction)

Mots-clés: oulankaïte, solution solide, sulfotellurure, éléments du groupe du platine, minéraux du groupe du platine, intrusion stratiforme, Lukkulaisvaara, Karélie russe, bouclier baltique.

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Introduction

Oulankaite, a complex stannosulfotelluride of Pd, Pt, Cu, and Fe, was reported as a new species of platinum-group mineral (PGM) from the Nadezhda ("Hope") Pd–Pt–Ag deposit, associated with the Lukkulaisvaara intrusion, Oulanka (or Olanga) group of intrusive complexes, northern Karelia, northwestern Russia (Barkov *et al.* 1996). Oulankaite [$(Pd,Pt)_5(Cu,Fe)_4SnTe_2S_2$] is the only species of stannosulfotelluride among the PGM (*cf.* Cabri 2002). Because it is finely twinned, its crystal structure remains undetermined; the powder X-ray-diffraction data (Barkov *et al.* 1996) suggest a tetragonal symmetry.

The extent of solid solution and element substitution was not established in the previous study. Here we report the compositional variations in oulankaite from the type occurrence on the basis of results of 1078 wavelength-dispersion (WDS) analyses, made on twenty-five grains. The new analytical results suggest a revised general formula for oulankaite. We also report the existence of a new compositional series of argentoan oulankaite, in which Ag substitutes for Cu. Considerable amounts of Ag can enter the *Cu* site, such that an unnamed Ag-dominant analogue appears to exist. As the type locality remains the only reported occurrence of oulankaite, its unusual and complex composition would appear to require a special environment of crystallization.

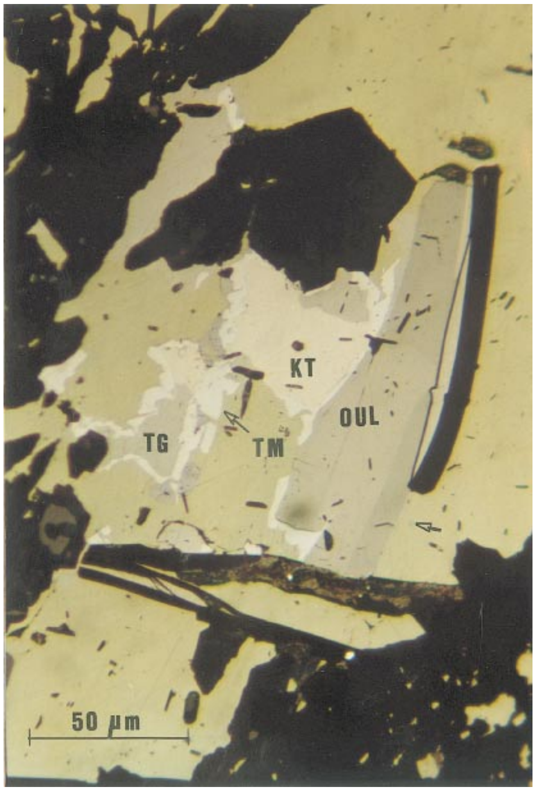
Occurrence and Associated Minerals

A large variety of PGM are associated with bodies of microgabbronorite in the Early Proterozoic Lukkulaisvaara layered intrusion, hosted by mafic rocks of the layered series (*e.g.,* Begizov & Batashev 1981, Grokhovskaya *et al.* 1992, Barkov *et al.* 1996, 1999, 2001, 2002). Oulankaite and other PGM occur in pods (<0.5 m across) and stringers of coarse-grained to pegmatitic gabbronorite, which locally grades to a plagioclase-bearing pyroxenite, located near the center of a sill-like body of microgabbronorite *ca.* 150 m thick. These pods are enriched in platinum-group elements, PGE (mostly Pd and, to a lesser degree, Pt) and Ag. They contain base-metal sulfides, and display various degrees of alteration; their primary texture and relics of igneous minerals are typically preserved, however. The igneous silicates of the PGM-bearing pods display the same range of composition as in the host microgabbronorite, thus implying a close genetic relationship and an apparent equilibrium between the mineralized pods and the host microgabbronorite. The PGE–Ag-rich pods contain enstatite: $Wo_{3.7–4.6}En_{74.7–76.5}Fs_{19.3–21.4}$ (~50 to 70 vol.%), plagioclase: $An_{68–59}$ (~10 to 40 vol.%), augite: $Wo_{41.1–43.4}En_{43.9–49.0}Fs_{9.9–12.7}$ (<10 vol.%), magnetite (up to ~10 vol.%) and minor quartz. Ferropargasite and a Cl-dominant analogue of ferropargasite (up to 4.5 wt.% Cl) are present as veinlets and rims on the igneous plagioclase, minute but locally abundant inclusions in chalcopyrite, oulankaite and other PGM, in staurolite, and in an intergrowth with Pd–Ag tellurides (Barkov *et al.* 2001). Almandine is common as a product of replacement of plagioclase. Interestingly, microcrystalline staurolite (≤0.3 mm), which occurs in intimate intergrowths with the Al–(Cl)-rich amphibole and almandine, formed at the expense of the primary plagioclase at a deuteric stage (Barkov *et al.* 1999). Epidote and chlorite have replaced plagioclase. Accessory hercynite (0.2 mm) is enriched in Zn. Phlogopite contains Cl (0.8 wt.%) and occurs as small (<40 μm) inclusions in chalcopyrite. Corundum (<0.1 mm) and a polymorph of Al_2SiO_5 (≤50 μm) are both very rare accessories; an AlO(OH) phase was observed as a rim around corundum. Actinolite, tremolite, cummingtonite or anthophyllite (or both) and talc are a common product of replacement of enstatite.

The PGE–Ag-rich pods and stringers are enriched in base-metal sulfide minerals (up to ~20–25 vol.%), mainly chalcopyrite, bornite, millerite, and pentlandite. Polydymite [$(Ni_{2.73}Fe_{0.23})_{\Sigma 2.96}S_{4.04}$] is common as a product of replacement of pentlandite. These pods and stringers contain various PGM, in addition to oulankaite, including telargpalite [$Pd_{2-x}Ag_{1+x}(Te,Bi)$], moncheite [$PtTe_2$], kotulskite [Pd(Te,Bi)], vysotskite–braggite [(Pd,Pt,Ni)S], tulameenite [Pt_2FeCu], sperrylite [$PtAs_2$], zvyagintsevite [Pd_3Pb], atokite–rustenburgite [$(Pd,Pt)_3Sn$], the intermetallic phase [$(Pd_{2.30}Cu_{0.46}Pt_{0.21}Fe_{0.02})_{\Sigma 2.99}Sn_{1.01}$ or $(Pd,Pt)_5(Cu,Fe)Sn_2$: *cf.* synthetic "stannopalladinite" of Evstigneeva & Nekrasov 1984], irarsite [IrAsS], telluropalladinite [Pd_9Te_4], and tarkianite [$(Cu,Fe)(Re,Mo)_4S_8$] (*e.g.*, Barkov & Lednev 1993, Barkov *et al.* 1996, 1999, 2001, Kojonen *et al.* 2004). Oulankaite and argentoan oulankaite are most closely associated with telargpalite, moncheite, kotulskite, irarsite, sperrylite, tulameenite (Figs. 1 to 4), and, as alluded to earlier, with Cl-rich calcic amphibole (up to 3.25 wt.% Cl) (Figs. 3D, 5, 6).

Optical Properties

The total of 25 grains of oulankaite, argentoan oulankaite and its Ag-dominant analogue have uniform and characteristic optical properties. Typically, they display a distinct to strong bireflectance, along with a moderate to strong anisotropy, with a reflection pleochroism in purplish pink, creamy pink or grayish cream tints. In reflected light, some of the oulankaite grains may resemble pyrrhotite (absent in these pods and stringers). Crystals of oulankaite typically have a platy habit, and the presence of fine twins of platy morphology in these crystals is characteristic (*e.g.*, Figs. 1–3A,C). The reflectance and color values for oulankaite and the Ag-dominant analogue of oulankaite are listed in Tables 1 to 3. The spectra of the two minerals are uniform, but differ significantly in reflectance values (Fig. 7). Previous measurements, made on a sample of Ag-poor oulankaite (Barkov *et al.* 1996), gave R_2 (max.) values



similar to those listed here for the Ag-dominant analogue of oulankaite. Thus, the reflectance values of oulankaite appear to depend more strongly on precise crystallographic orientation than on composition.

Analytical Methods

In this study, several independent sets of electron-microprobe analyses were obtained using different methods (wavelength-dispersion, WDS, and energy-dispersion, EDS), in different laboratories, with different analytical conditions and standards. The quantitative EDS analyses were carried out using a JEOL JSM–6400 scanning-electron microscope equipped with a LINK eXL energy-dispersion spectrometer. The analytical conditions were 15 kV and 1.2 nA, ~1 µm beam size, 100 s count times, and the following X-ray lines: Pd*L*, Pt*M*, Cu*K*, Fe*K*, Ag*L*, Sn*L*, Te*L*, and S*K*. Pure elements, synthetic $PtTe_2$ and $CuFeS_2$ were used as standards. The

FIG. 1. Reflected-light microphotograph showing oulankaite (OUL) in association with kotulskite, KT [$(Pd_{1.00}Pt_{0.01}Ni_{<0.01})(Te_{0.64}Bi_{0.34}Sb_{<0.01})$], telargpalite (TG) and tulameenite, TM [$Pt_{1.93}Fe_{1.04}(Cu_{0.92}Ni_{0.10})_{\Sigma 1.02}$] from the Lukkulaisvaara intrusion, northern Russian Karelia. The host base-metal sulfide is chalcopyrite; silicate minerals are black. Note the presence of a fine and platy twin in the oulankaite (shown by the black arrow).

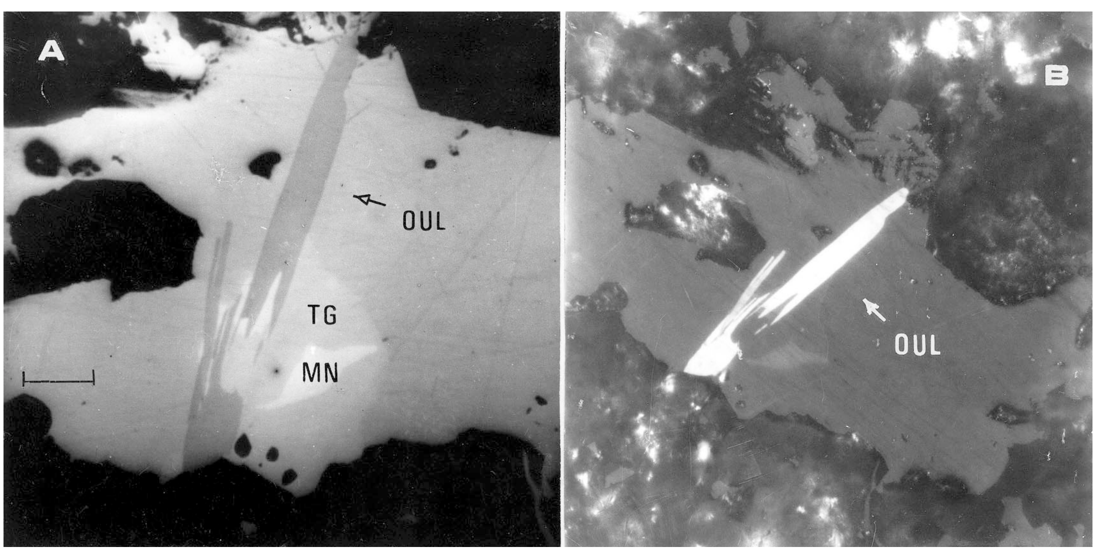


FIG. 2. A. Grains of argentoan oulankaite (OUL) in association with telargpalite (TG) and moncheite (MN) from the Lukkulaisvaara intrusion: reflected-light microphotograph taken with partly crossed nicols. The host base-metal sulfide is chalcopyrite. B. The same grains (OUL) show a strong anisotropy: reflected-light microphotograph taken with crossed nicols. Scale bar (shown in A) equals 20 µm.

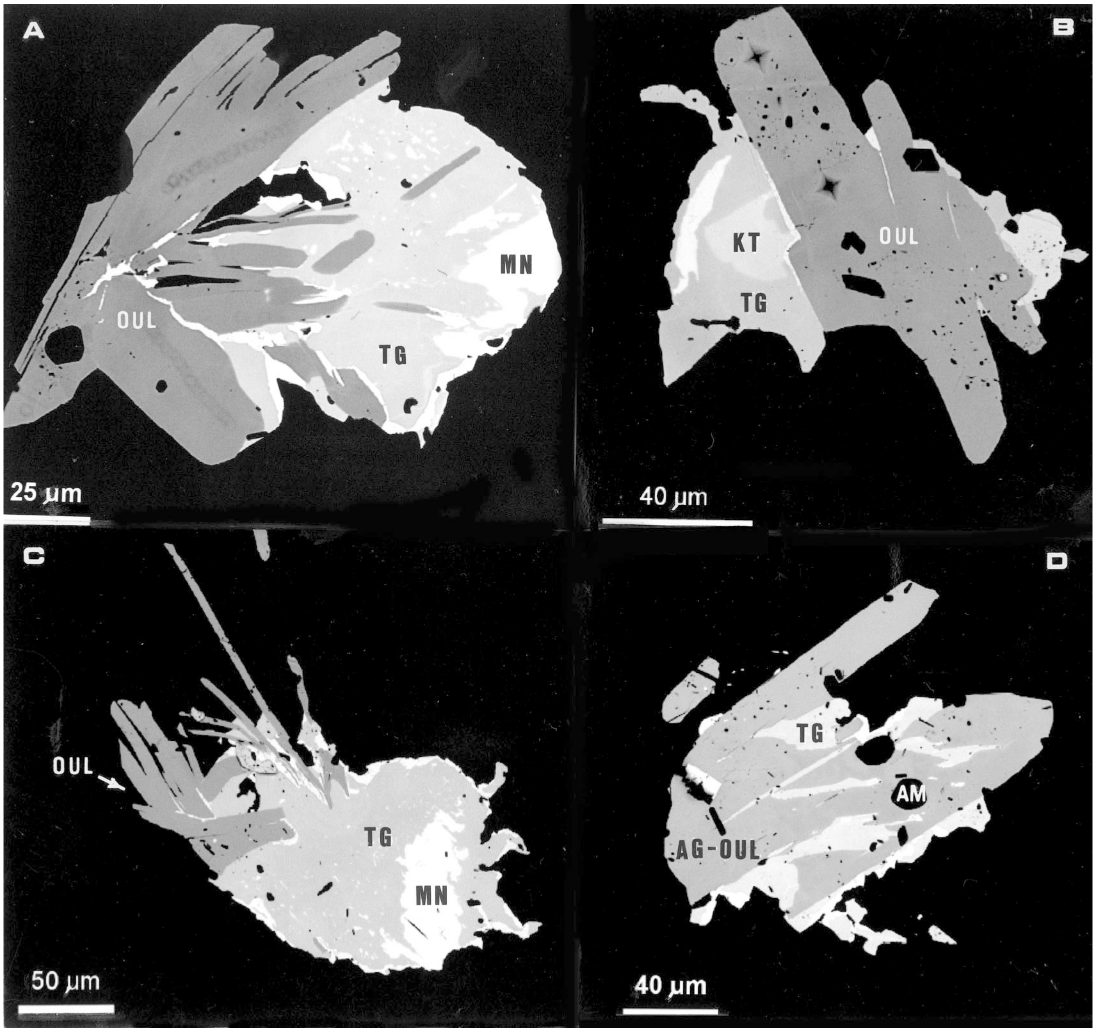


FIG. 3. A–C. Examples of grains of oulankaite (OUL) displaying intergrowth relationships with various PGM: telargpalite (TG), moncheite (MN), kotulskite (KT), and irarsite [$(Ir_{0.82}Pt_{0.11}Rh_{0.05})_{\Sigma 0.98}As_{1.03}S_{0.98}$: a tiny grain shown in Figure 3C, which is *ca.* 25 µm in length, and is in contact with the oulankaite]. Tulameenite occurs as a thin rim around telargpalite (Fig. 3A). D. A large grain of argentoan oulankaite (AG–OUL), which displays considerable variations in concentration of Ag (5.4 to 12.2 wt.% Ag) and is closely associated with telargpalite (TG) and a Cl-rich amphibole, AM: up to 3.25 wt.% Cl (Table 4). In all cases (A–D), the host mineral is chalcopyrite. A–D: back-scattered electron images.

EDS spectra were processed with a ZAF on-line program. The estimated errors were Pd 0.3, Pt 0.1, Cu 0.4, Sn 0.2, and S 0.1 wt.%. The observed totals (not normalized) are close to 100 wt.%.

A Cameca Camebax electron microprobe was operated at an accelerating voltage of 20 kV and a probe current of 22 nA. The following X-ray lines and standards were used: Pd*L*α (pure Pd), Pt*M*α (synthetic PtSn), Cu*K*α (pure Cu), Fe*K*α (FeS_2), Ag*L*β (pure Ag), Sn*L*α (PtSn), Te*L*α (PdBiTe), and S*K*α (FeS_2). The results were processed with a PAP on-line program. A correction for the interference between the Pd*L* and Ag*L* emission lines was made.

A JEOL JXA–8900 electron microprobe was operated at 20 kV and 20 nA, and the following X-ray lines and standards were used: Pd*L*α, Pt*L*α (pure metals), Cu*K*α, Fe*K*α, S*K*α ($CuFeS_2$), Ag*L*β ($AgBiSe_2$), Sn*L*α (SnO_2), and Te*L*α (PbTe). The results were processed with a ZAF (JEOL) on-line program, and a correction for the interference between the Pd*L* and Ag*L* lines was

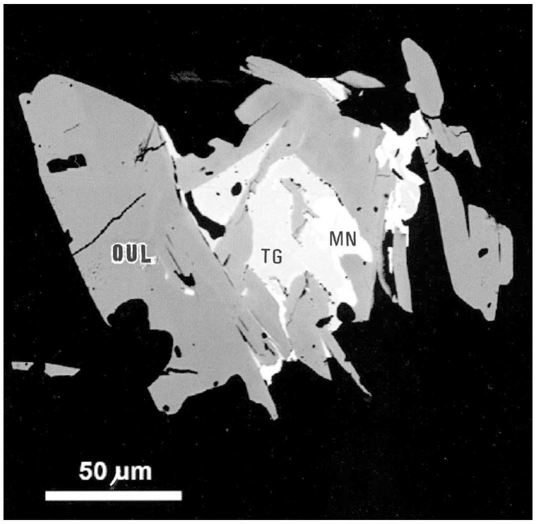


FIG. 4. A large intergrowth of oulankaite (OUL) with telargpalite (TG) and moncheite (MN). The host mineral is chalcopyrite. Back-scattered electron image.

TABLE 1. REFLECTANCE VALUES OF OULANKAITE AND Ag-DOMINANT ANALOGUE OF OULANKAITE FROM LUKKULAISVAARA, KARELIA, RUSSIA

	Ag-poor oulankaite [§]				Ag-dominant analogue of oulankaite *			
λ nm	R_1% (air)	R_2% (air)	R_1% (oil)	R_2% (oil)	R_1% (air)	R_2% (air)	R_1% (oil)	R_2% (oil)
400	31.8	31.2	22.7	23.0	35.5	37.5	21.9	25.7
420	32.0	31.9	23.0	23.7	36.0	37.8	22.0	26.2
440	32.3	32.4	23.3	25.2	37.7	40.5	22.8	28.2
460	32.4	34.5	23.4	26.6	39.8	43.2	23.9	30.8
470	32.5	35.0	23.5	27.0	40.5	44.1	24.2	31.9
480	32.7	36.4	23.8	27.7	41.8	45.4	24.9	33.3
500	33.0	37.4	24.1	28.2	42.8	46.9	25.5	34.9
520	33.9	38.8	25.1	29.3	43.8	48.0	26.2	35.9
540	34.8	40.1	26.1	30.4	44.7	49.3	27.0	37.4
546	35.0	40.3	26.1	30.5	45.0	49.5	27.2	38.1
560	35.6	41.1	26.5	30.9	45.6	50.4	27.7	38.5
580	36.4	42.0	27.2	31.9	45.9	51.3	28.2	39.6
589	36.6	42.3	27.3	32.1	46.0	52.0	28.2	40.1
600	36.9	42.8	27.6	32.8	46.2	52.5	28.5	40.9
620	37.3	43.4	27.6	33.5	46.2	53.0	28.6	41.3
640	37.4	43.5	27.7	33.6	46.0	53.5	28.7	41.7
650	37.4	43.6	27.8	33.7	45.8	53.5	28.8	41.7
660	37.6	43.7	28.0	33.9	45.7	53.6	28.8	41.7
680	37.9	43.7	28.0	33.9	45.5	53.8	28.9	41.8
700	38.5	43.7	28.4	34.2	45.2	53.9	29.0	41.8

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

[§] The composition of this Ag-free oulankaite is $(Pd_{5.00}Pt_{0.18})_{\Sigma 5.18}$ $(Cu_{3.40}Fe_{0.56})_{\Sigma 3.96}$ $Sn_{0.92}Te_{1.97}S_{1.97}$ (anal. 9, Table 5).

* The composition of the Ag-dominant analogue of oulankaite is $(Pd_{5.39}Pt_{0.15})_{\Sigma 5.54}$ $(Ag_{1.42}Cu_{1.24}Fe_{0.63})_{\Sigma 3.29}$ $Sn_{1.03}Te_{2.12}S_{2.02}$ (anal. 3, Table 9).

made. Concentrations of Ni, Co, Au, Bi, Sb, and As were found to be below the limit of detection (WDS) in all of the grains of oulankaite and argentoan oulankaite investigated.

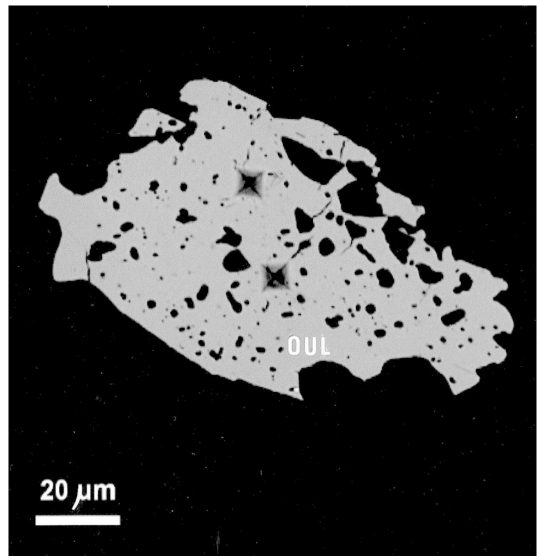


FIG. 5. Oulankaite (OUL) located at the contact of chalcopyrite and a Cl-rich ferropargasite (1.7–2.2 wt.% Cl) and containing abundant inclusions (black) of a Cl-rich ferropargasite (1.8–2.1 wt.% Cl). Back-scattered electron image.

TABLE 2. COLOR VALUES (*C* illuminant) OF OULANKAITE FROM THE LUKKULAISVAARA INTRUSION, KARELIA, RUSSIA

		x	y	Y %	P_e%	λ_d
in air	R_1	0.322	0.326	35.4	5.9	581
in air	R_2	0.330	0.338	40.6	11.2	577
in oil	R_1	0.325	0.329	26.3	7.6	580
in oil	R_2	0.330	0.336	30.9	10.7	578

Reflectance values in air and in oil are given in Table 1.

TABLE 3. COLOR VALUES (*C* illuminant) OF Ag-DOMINANT ANALOGUE OF OULANKAITE FROM LUKKULAISVAARA

		x	y	Y %	P_e%	λ_d
in air	R_1	0.323	0.334	44.9	8.1	574
in air	R_2	0.328	0.336	50.0	10.4	576
in oil	R_1	0.326	0.334	27.3	9.2	576
in oil	R_2	0.336	0.344	38.1	14.4	576

Reflectance values in air and in oil are given in Table 1.

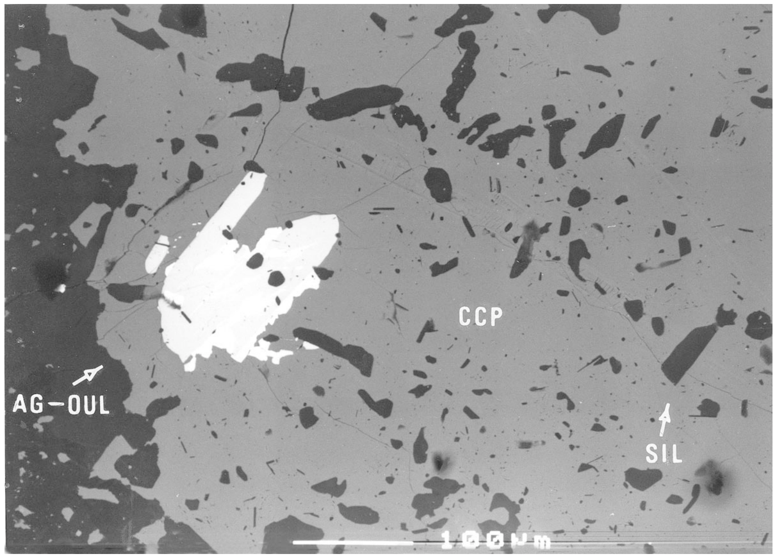


FIG. 6. The association of argentoan oulankaite (AG–OUL: grain shown in Fig. 3D) with hydrous silicates (SIL) and chalcopyrite (CCP). Back-scattered electron image.

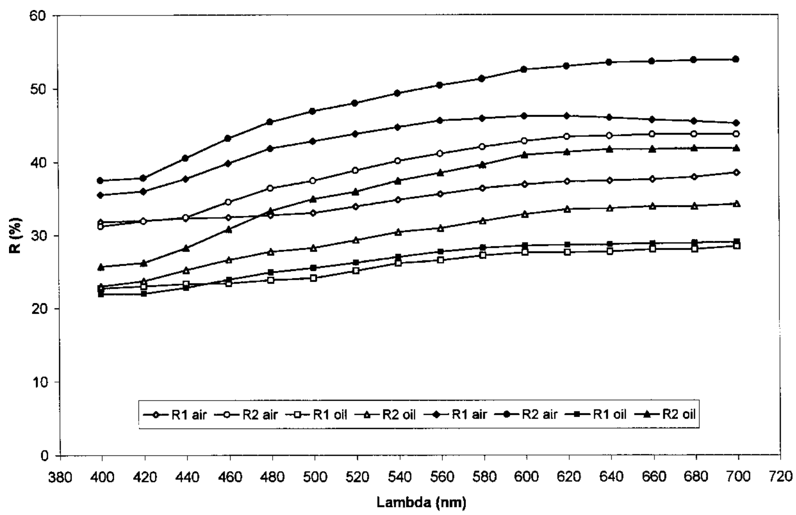


FIG. 7. Reflectance spectra for oulankaite (open symbols) and the Ag-dominant analogue of oulankaite (filled symbols) from the Lukkulaisvaara intrusion. The reflectance was measured in air and in oil; values (*R* %) are plotted *versus* wavelength λ in nm.

Results and Discussion

Variations observed in Ag-poor and Ag-rich oulankaite on the basis of results of EDS analyses

A total of 90 quantitative EDS analyses (hereafter: *n* = 90) of Ag-poor or Ag-free oulankaite were made on ten grains. The mean composition corresponds to the formula $(Pd_{5.05}Pt_{0.19})_{\Sigma 5.24}(Cu_{3.13}Fe_{0.58})_{\Sigma 3.71}Sn_{0.99}Te_{2.13}S_{1.93}$ (Σatoms = 14). In terms of atoms per formula unit (*apfu*), the following ranges were observed in this dataset: Pd 4.80–5.45, Pt 0.07–0.29, Cu 2.61–3.44, Fe 0.49–0.69, Sn 0.93–1.05, Te 2.04–2.19, and S 1.88–1.99. The (Pd + Pt) value varies from 5.03 to 5.63, with a mean of 5.24, and the (Cu + Fe + Ag) value varies from 3.23 to 4.00, with a mean of 3.71 *apfu*. The ΣMe value (*i.e.*, Pd + Pt + Cu + Fe + Ag) ranges between 8.86 and 9.05 *apfu*. Pd displays a well-defined negative correlation with Cu; the correlation coefficient R is –0.92, which clearly implies the existence of a Pd-for-Cu substitution. Correlations of Pt–Pd (R = –0.52) and Fe–Cu (R = –0.64) both are weak and negative, consistent with the incorporation of minor Pt and Fe in the *Pd* site and *Cu* site, respectively. There is a strong negative correlation (R = –0.97) between the values (Pd + Pt) and (Cu + Fe + Ag), expressed in *apfu*. The concentrations of Te and S do not correlate. However, the compositions in this dataset typically exhibit a slight excess in Te, the average being 2.13 Te *apfu*, which is coupled with a corresponding deficit in S (1.93 *apfu*: n = 90). This characteristic implies the incorporation of *ca.* 0.1 *apfu* of the "excess amount" of Te at the *S* site. Minor amounts of Te replace S in vasilite [$(Pd,Cu)_{16}(S,Te)_7$: Atanasov 1990] and in synthetic $CuRh_2(S_{1-x}Te_x)_4$ ($0 \le x \le 0.1$: Kijima *et al.* 1996), for example.

The EDS data on argentoan oulankaite (n = 42: three grains) gave the following mean composition: $(Pd_{5.25}Pt_{0.15})_{\Sigma 5.40}(Cu_{1.86}Ag_{1.09}Fe_{0.61})_{\Sigma 3.56}Sn_{1.00}Te_{2.12}S_{1.93}$ (Σatoms = 14). The following ranges in *apfu* are found: Pd 5.12–5.37, Pt 0.11–0.18, Cu 1.41–2.59, Fe 0.55–0.72, Ag 0.42–1.63, Sn 0.96–1.05, Te 2.06–2.16, and S 1.88–2.00. The (Pd + Pt) value ranges from 5.30 to 5.51, with a mean of 5.39 *apfu*, and the (Cu + Fe + Ag) value ranges from 3.41 to 3.73, with a mean of 3.56 *apfu*. The ΣMe values are tightly constrained (8.89–9.08 *apfu*). A strong negative correlation (R = –0.97) exists between contents of Cu and Ag and clearly indicates that Ag replaces Cu in the structure. It is noteworthy that Pd does not correlate with either Cu or Ag in this dataset. As before, the (Pd + Pt) value correlates negatively with the (Cu + Fe + Ag) value: R = –0.88.

The following EDS composition of Ag-dominant analogue of oulankaite (Fig. 3D) is representative: Pd 41.94, Pt 1.72, Ag 13.02, Cu 7.25, Fe 2.53, Sn 8.74, Te 20.32, S 4.67, and total 100.19 wt.%, giving an empirical formula of $(Pd_{5.20}Pt_{0.12})_{\Sigma 5.32}(Ag_{1.59}Cu_{1.50}Fe_{0.60})_{\Sigma 3.69}Sn_{0.97}Te_{2.10}S_{1.92}$; here, the estimated error for Ag is 0.4 wt.%. These data also suggest that *ca.* 0.1 Te *apfu* may enter the *S* site.

TABLE 4. ELECTRON-MICROPROBE DATA ON MICRO-INCLUSIONS OF Cl-RICH AMPHIBOLE IN ARGENTOAN OULANKAITE, LUKKULAISVAARA

No.	1	2		1	2
SiO_2 wt.%	37.41	37.27	Si *apfu*	5.88	5.93
TiO_2	0.01	n.d.	^{IV}Al	2.12	2.07
Al_2O_3	16.25	14.60	^{VI}Al	0.89	0.67
Cr_2O_3	0.01	0.05	Fe	2.57	2.76
FeO	19.58	20.74	Mg	1.44	1.45
MnO	0.07	0.08	Mn	0.01	0.01
MgO	6.17	6.12	Ni	0.03	0.03
NiO	0.21	0.21	Ti	<0.01	-
CaO	11.42	11.38	Cr	<0.01	<0.01
Na_2O	1.64	1.66	Ca	1.92	1.94
K_2O	1.27	1.45	Na	0.50	0.51
Cl	2.85	3.25	K	0.25	0.29
O≡Cl	0.64	0.73	Cl	0.76	0.88
Total	96.25	96.08	*mg#*	35.97	34.47

Analyses 1 and 2: micro-inclusions of Cl-rich amphibole shown in Figure 3D. All Fe is expressed as FeO. The wavelength-dispersion electron-microprobe analyses were carried out using a Cameca Camebax microprobe. The analytical conditions were 22 kV and 20 nA, and vanadinite was used as the standard for Cl. The number of cations was calculated on the basis of O = 23. $mg\# = 100\ Mg / (Mg + Fe)$.

Variations observed in Ag-poor oulankaite on the basis of results of WDS analyses

Significant deviations from the ideal formula of oulankaite are documented by results of 24 WDS analyses (Cameca Camebax microprobe: Tables 5 and 6). Figure 8 shows that the values (Pd + Pt) and (Cu + Fe + Ag) vary from 5.16 to 5.73, with a mean of 5.37 *apfu*, and from 2.99 to 4.00, with a mean of 3.59 *apfu*, respectively, and are inversely correlated (R = –0.99). The correlation of Pd and Cu is also strongly negative (R = –0.98: Fig. 9). The ΣMe value varies from 8.68 to 9.18, with a mean value of 8.96 *apfu*. The average formula, derived from this set of analyses, is $(Pd_{5.20}Pt_{0.18})_{\Sigma 5.38}(Cu_{2.96}Fe_{0.61}Ag_{0.01})_{\Sigma 3.58}Sn_{0.97}Te_{2.05}S_{2.02}$ (n = 24: Tables 5, 6).

Representative results of a larger dataset (n = 835), made on 20 grains of Ag-poor oulankaite, are presented in Tables 7 and 8. These results gave the following average composition and the ranges (in wt.%): Pd 42.62 (40.70–45.04), Pt 3.02 (1.77–4.24), Cu 15.98 (12.87–17.84), Fe 2.65 (2.34–3.77), Ag 0.01 (0.00–0.24), Sn 9.96 (9.06–10.33), Te 21.17 (20.10–21.77), S 5.25 (5.05–5.43), and total 100.66, and a formula of $(Pd_{4.97}Pt_{0.19})_{\Sigma 5.16}(Cu_{3.12}Fe_{0.59}Ag_{0.001})_{\Sigma 3.71}Sn_{1.04}Te_{2.06}S_{2.03}$ (Σatoms = 14). In terms of *apfu*, the observed variations are Pd 4.77–5.34, Pt 0.11–0.27, Cu 2.58–3.42, Fe 0.52–0.85, Ag 0.00–0.03, Sn 0.95–1.10, Te 1.99–2.13, and S 1.96–2.11. The (Pd + Pt) value ranges from 4.95 to 5.51, with a mean value of 5.16 *apfu*, and the (Cu + Fe + Ag) value varies within the range 3.26 – 4.00, with a mean of 3.71 *apfu*. A strong negative correlation (R = –0.96) is observed between these values (Fig. 8). The Pd–Cu correlation is also strongly negative (R = –0.86: Fig. 9). The ΣMe value varies from 8.70 to 9.00, with a mean of 8.87 *apfu*. In contrast to the EDS data, no deficit in S is displayed by the compositions in these datasets (WDS). In addition, several WDS analyses suggest that minor In is present in oulankaite: up to 0.48 wt.% (0.05 *apfu* In), and probably reflects a minor In-for-Sn substitution. The observed contents of In are unlikely to be analytical artifacts, because they are negatively correlated with the amount of Sn.

Variations observed in argentoan oulankaite on the basis of results of WDS analyses

Some of the 25 grains analyzed in the present study were found to contain levels of Ag above the "background" values of <0.1–0.3 wt.% (WDS data). The results of WDS analyses are listed in Tables 9 and 10 (Cameca Camebax microprobe: n = 28). There are sig-

TABLE 5. CHEMICAL COMPOSITION[§] OF Ag-POOR OULANKAITE FROM THE LUKKULAISVAARA INTRUSION, KARELIA, RUSSIA

	Pd	Pt	Cu	Fe	Ag	Sn	Te	S	Total
1	42.58	2.86	16.96	2.46	n.d.	9.24	20.10	5.08	99.28
2	42.49	2.71	17.07	2.51	0.05	9.19	20.15	4.95	99.12
3	42.80	2.46	17.37	2.50	0.12	9.13	20.06	5.06	99.50
4	42.83	2.57	17.29	2.45	n.d.	9.09	20.22	5.02	99.47
5	42.99	2.92	16.96	2.43	0.08	8.81	20.11	5.09	99.39
6	42.41	3.26	17.16	2.80	n.d.	8.81	19.76	5.04	99.24
7	42.71	2.99	17.51	2.50	n.d.	8.87	19.98	5.04	99.60
8	42.74	2.85	17.07	2.40	0.06	8.76	20.08	5.00	98.96
9	42.75	2.83	17.35	2.52	n.d.	8.77	20.15	5.08	99.45
10	42.95	2.92	15.21	2.82	0.45	8.76	20.82	5.01	98.94
11	43.36	2.34	15.37	2.76	0.20	8.64	20.90	5.05	98.62
12	43.07	2.33	15.82	2.85	n.d.	8.65	20.87	5.10	98.69
13	44.01	2.27	15.12	3.11	0.66	8.65	20.71	5.10	99.63
14	43.20	2.78	15.29	2.87	0.16	8.51	20.71	5.04	98.56
15	42.56	3.28	15.36	2.77	0.12	8.65	20.76	5.04	98.54
16	42.82	3.49	15.47	2.69	0.09	8.66	20.58	5.10	98.90
17	45.20	2.61	12.25	3.04	0.07	9.73	21.16	5.26	99.32
18	45.64	2.68	11.73	2.76	0.09	9.66	21.34	5.26	99.16
19	46.05	2.57	11.80	2.64	n.d.	9.71	21.25	5.23	99.25
20	45.53	2.70	11.67	2.69	0.09	9.67	21.21	5.17	98.73
21	44.54	2.59	12.03	2.96	0.08	9.57	21.29	5.22	98.28
22	45.04	2.68	12.16	3.09	0.07	9.65	21.36	5.31	99.36
23	45.45	2.66	11.78	2.72	0.11	9.81	21.15	5.30	98.98
24	45.45	2.39	12.21	2.64	0.07	9.69	21.31	5.23	98.99
*25**	43.72	2.74	14.92	2.71	0.11	9.11	20.67	5.12	99.10

§ Cameca Camebax electron microprobe; results quoted in wt.%. n.d.: not detected.
* The average results of the analyses (1 to 24).

TABLE 6. ATOMIC PROPORTIONS[§] (ΣATOMS = 14) OF Ag-POOR OULANKAITE FROM THE LUKKULAISVAARA INTRUSION, KARELIA, RUSSIA

	Pd	Pt	ΣPd, Pt	Cu	Fe	Ag	ΣCu, Fe, Ag	ΣMe	Sn	Te	S
1	5.00	0.18	5.18	3.34	0.55	-	3.89	9.07	0.97	1.97	1.98
2	5.00	0.17	5.17	3.37	0.56	<0.01	3.94	9.11	0.97	1.98	1.93
3	5.00	0.16	5.16	3.40	0.56	0.01	3.97	9.13	0.96	1.95	1.96
4	5.02	0.16	5.18	3.39	0.55	-	3.94	9.12	0.95	1.98	1.95
5	5.05	0.19	5.24	3.33	0.54	<0.01	3.88	9.12	0.93	1.97	1.98
6	4.97	0.21	5.18	3.37	0.63	-	4.00	9.18	0.93	1.93	1.96
7	4.99	0.19	5.18	3.43	0.56	-	3.99	9.17	0.93	1.95	1.96
8	5.04	0.18	5.22	3.37	0.54	<0.01	3.92	9.14	0.93	1.98	1.96
9	5.00	0.18	5.18	3.40	0.56	-	3.96	9.14	0.92	1.97	1.97
10	5.11	0.19	5.30	3.03	0.64	0.05	3.72	9.02	0.93	2.07	1.98
11	5.15	0.15	5.30	3.06	0.63	0.02	3.71	9.01	0.92	2.07	1.99
12	5.09	0.15	5.24	3.13	0.64	-	3.77	9.01	0.92	2.06	2.00
13	5.17	0.15	5.32	2.98	0.70	0.08	3.76	9.08	0.91	2.03	1.99
14	5.14	0.18	5.32	3.05	0.65	0.02	3.72	9.04	0.91	2.06	1.99
15	5.08	0.21	5.29	3.07	0.63	0.01	3.71	9.00	0.93	2.07	2.00
16	5.09	0.23	5.32	3.08	0.61	0.01	3.70	9.02	0.92	2.04	2.01
17	5.42	0.17	5.59	2.46	0.69	<0.01	3.16	8.75	1.05	2.11	2.09
18	5.51	0.18	5.69	2.37	0.63	0.01	3.01	8.70	1.05	2.15	2.11
19	5.56	0.17	5.73	2.38	0.61	-	2.99	8.72	1.05	2.14	2.09
20	5.53	0.18	5.71	2.37	0.62	0.01	3.00	8.71	1.05	2.15	2.08
21	5.40	0.17	5.57	2.44	0.68	0.01	3.13	8.70	1.04	2.15	2.10
22	5.39	0.18	5.57	2.44	0.71	<0.01	3.16	8.73	1.04	2.13	2.11
23	5.49	0.18	5.67	2.38	0.63	0.01	3.02	8.69	1.06	2.13	2.12
24	5.48	0.16	5.64	2.47	0.61	<0.01	3.09	8.73	1.05	2.14	2.09
*25**	5.20	0.18	5.38	2.96	0.61	0.01	3.58	8.96	0.97	2.05	2.02

§ The analytical results (in wt.%) are listed in Table 5 (Cameca Camebax microprobe).
* The average results of the analyses (1 to 24).

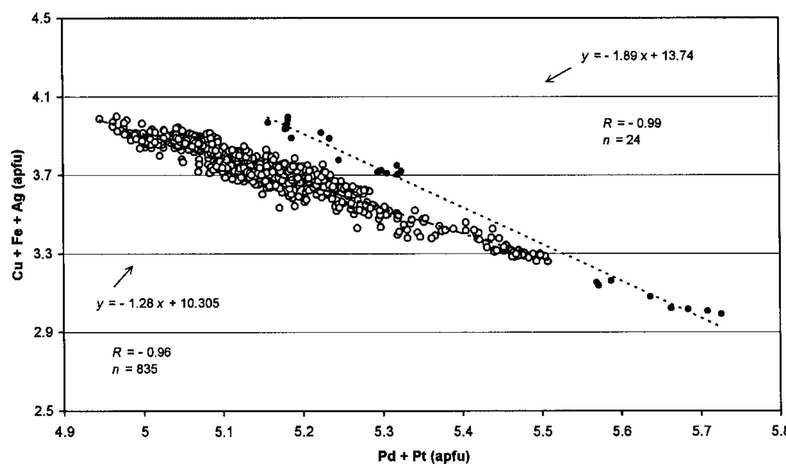


FIG. 8. Compositional variation of Ag-poor oulankaite from the Lukkulaisvaara layered intrusion, northern Russian Karelia, in terms of the plot of (Cu + Fe + Ag) *versus* (Pd + Pt) (in atoms per formula unit, *apfu*; Σatoms = 14). Results of eight hundred and thirty-five WDS analyses (JEOL–8900 electron microprobe: open circles) and twenty-four WDS analyses (Cameca Camebax electron microprobe: filled circles) are plotted.

nificant antipathetic covariations in Ag and Cu, and a strong negative correlation ($R = -0.97$) is observed between the amounts of these elements, consistent with Ag-for-Cu substitution (Fig. 10). Similar to other PGM at Nadezhda, grains of argentoan oulankaite may contain inclusions of Cl-rich ferropargasite (Fig. 3D). Wide variations in Ag and Cu contents are observed in a grain of argentoan oulankaite (Fig. 3D), which consists of Ag-enriched zones (*ca.* 10 to 20 μm in size) with up to 12.2 wt.% Ag, corresponding to the composition $(Pd_{5.31}Pt_{0.17})_{\Sigma 5.48}(Ag_{1.52}Cu_{1.27}Fe_{0.63})_{\Sigma 3.42}Sn_{1.03}Te_{2.09}S_{1.98}$ (anal. 8, Table 9), similar to that derived from the EDS data. Thus on the basis of the ideal formula of oulankaite, this phase would appear to be an unnamed species of PGM. It was not possible to characterize it further, owing to the small size of the grains and the Ag-rich zones. It remains unknown if the maximum content of Ag encountered (1.5 Ag *apfu*: WDS data, and 1.6 Ag *apfu*: EDS data) is the upper limit of Ag-for-Cu substitution.

The mean composition of argentoan oulankaite in the present dataset is $(Pd_{5.38}Pt_{0.14})_{\Sigma 5.52}(Cu_{1.45}Ag_{1.23}Fe_{0.64})_{\Sigma 3.32}Sn_{1.02}Te_{2.10}S_{2.03}$, with Cu slightly dominant over Ag. The values (Pd + Pt) and (Cu + Fe + Ag) range from 5.42 to 5.63 *apfu*, and 3.18 to 3.42 *apfu*, respectively, and display a well-defined negative correlation ($R = -0.82$). As shown in Figure 11, both (Pd + Pt) and (Cu + Fe + Ag) display significant deviations from the ideal proportions of oulankaite, suggesting that the Ag-for-Cu substitution is combined with a more complex substitution of Pd for Cu + Ag (+Fe).

Representative results of another dataset, based on 188 point analyses of argentoan oulankaite (WDS: JEOL–8900 microprobe), are listed in Tables 11 and 12. The Ag-bearing compositions having at least 0.25 wt.% Ag are included in this dataset. The mean composition and the observed ranges are the following (in wt.%): Pd 42.78 (41.00–43.92), Pt 2.33 (1.59–4.26), Cu 10.52 (7.05–16.63), Fe 2.66 (2.43–3.05), Ag 6.14 (0.25–11.68), Sn 9.78 (9.12–10.30), Te 20.66 (19.89–21.46),

TABLE 7. CHEMICAL COMPOSITION[§] OF Ag-POOR OULANKAITE FROM THE LUKKULAISVAARA INTRUSION, KARELIA, RUSSIA

	Pd	Pt	Cu	Fe	Ag	Sn	Te	S	Total
1	41.34	2.98	17.25	2.40	n.d.	9.84	21.28	5.18	100.27
2	42.08	2.63	17.39	2.40	n.d.	9.88	21.24	5.23	100.85
3	42.03	2.78	17.53	2.53	n.d.	9.93	21.26	5.21	101.27
4	44.24	2.56	13.36	3.34	n.d.	10.03	20.72	5.07	99.32
5	42.08	2.53	17.25	2.49	n.d.	9.97	21.48	5.25	101.05
6	41.58	2.74	17.11	2.48	n.d.	9.89	21.40	5.26	100.46
7	41.71	3.54	16.65	2.57	n.d.	9.94	21.10	5.20	100.71
8	42.43	2.78	16.30	2.59	n.d.	9.91	21.26	5.29	100.56
9	43.06	2.60	15.13	2.77	n.d.	10.02	21.11	5.23	99.92
10	43.33	3.41	14.77	2.73	n.d.	10.06	21.10	5.29	100.69
11	44.70	2.64	13.60	2.73	n.d.	10.06	21.12	5.22	100.07
12	44.83	2.65	13.49	2.71	n.d.	10.07	21.33	5.21	100.29
13	45.04	2.69	13.48	2.72	n.d.	10.07	21.19	5.22	100.41
14	42.84	2.45	16.97	2.39	n.d.	10.16	20.87	5.10	100.78
15	42.89	2.44	17.15	2.80	n.d.	10.01	21.11	5.22	101.62
16	42.20	2.76	17.40	2.45	n.d.	10.04	20.99	5.10	100.94
17	43.50	2.03	16.41	2.57	n.d.	9.89	21.14	5.15	100.69
18	42.59	3.46	16.13	2.59	n.d.	9.88	21.01	5.24	100.90
19	43.45	2.63	15.61	2.87	n.d.	9.87	20.90	5.21	100.54
20	43.40	2.08	16.56	2.64	n.d.	9.96	21.14	5.32	101.10
21	44.15	2.56	13.28	2.90	n.d.	10.03	20.90	5.17	98.99
22	44.93	2.56	13.53	2.73	n.d.	10.21	21.28	5.23	100.47
23	41.95	2.95	16.80	2.36	n.d.	9.70	20.94	5.29	99.99
24	41.50	3.17	17.05	2.58	n.d.	9.96	21.25	5.31	100.82
25	43.63	2.03	16.44	2.60	n.d.	9.98	21.00	5.29	100.97
26	43.12	2.68	16.05	2.66	n.d.	9.80	20.94	5.24	100.49
27	41.48	3.03	17.04	2.40	n.d.	10.03	21.04	5.25	100.27
28	41.27	3.11	17.33	2.71	n.d.	9.80	21.25	5.29	100.76
29	44.80	2.62	13.51	2.75	n.d.	10.04	21.25	5.23	100.20
30	44.68	2.67	13.90	3.07	n.d.	10.13	21.22	5.19	100.86
31	43.01	3.31	15.97	2.57	n.d.	9.91	20.91	5.18	100.86
32	42.84	2.54	17.31	2.50	n.d.	9.91	20.97	5.18	101.25
33	44.05	2.82	13.46	3.05	n.d.	9.95	20.91	5.15	99.39
34	41.53	3.20	17.23	2.63	n.d.	10.05	21.30	5.27	101.21
35	43.36	3.36	14.68	2.73	n.d.	10.07	21.22	5.20	100.62
36	44.15	2.67	15.69	2.60	n.d.	9.96	21.13	5.27	101.47
37	44.44	2.66	14.15	3.20	n.d.	10.17	21.20	5.30	101.12
38	43.55	3.36	14.46	2.70	n.d.	10.20	21.34	5.24	100.85
39	43.68	3.34	13.97	2.76	n.d.	10.17	21.39	5.33	100.64
40	41.61	3.18	17.20	2.64	n.d.	9.93	21.21	5.30	101.07

TABLE 8. ATOMIC PROPORTIONS[§] (ΣATOMS = 14) OF Ag-POOR OULANKAITE FROM THE LUKKULAISVAARA INTRUSION, KARELIA, RUSSIA

	Pd	Pt	ΣPd, Pt	Cu	Fe	Ag	ΣCu, Fe, Ag	Σ*Me*	Sn	Te	S
1	4.82	0.19	5.01	3.37	0.53	-	3.90	8.91	1.03	2.07	2.00
2	4.86	0.17	5.03	3.37	0.53	-	3.90	8.93	1.02	2.05	2.01
3	4.84	0.17	5.01	3.38	0.55	-	3.93	8.94	1.02	2.04	1.99
4	5.27	0.12	5.39	2.67	0.76	-	3.43	8.82	1.07	2.06	2.01
5	4.85	0.16	5.01	3.33	0.55	-	3.88	8.89	1.03	2.07	2.01
6	4.83	0.17	5.00	3.33	0.55	-	3.88	8.88	1.03	2.07	2.03
7	4.86	0.22	5.08	3.25	0.57	-	3.82	8.90	1.04	2.05	2.01
8	4.94	0.18	5.12	3.18	0.57	-	3.75	8.87	1.03	2.06	2.04
9	5.06	0.17	5.23	2.98	0.62	-	3.60	8.83	1.06	2.07	2.04
10	5.08	0.22	5.30	2.90	0.61	-	3.51	8.81	1.06	2.07	2.06
11	5.30	0.17	5.47	2.70	0.62	-	3.32	8.79	1.07	2.09	2.05
12	5.31	0.17	5.48	2.68	0.61	-	3.29	8.77	1.07	2.11	2.05
13	5.33	0.17	5.50	2.67	0.61	-	3.28	8.78	1.07	2.09	2.05
14	4.97	0.16	5.13	3.30	0.53	-	3.83	8.96	1.06	2.02	1.97
15	4.91	0.15	5.06	3.29	0.61	-	3.90	8.96	1.03	2.02	1.99
16	4.88	0.17	5.05	3.37	0.54	-	3.91	8.96	1.04	2.03	1.96
17	5.05	0.13	5.18	3.19	0.57	-	3.76	8.94	1.03	2.05	1.98
18	4.96	0.22	5.18	3.15	0.57	-	3.72	8.90	1.03	2.04	2.03
19	5.07	0.17	5.24	3.05	0.64	-	3.69	8.93	1.03	2.03	2.02
20	5.00	0.13	5.13	3.20	0.58	-	3.78	8.91	1.03	2.03	2.03
21	5.29	0.17	5.46	2.66	0.66	-	3.32	8.78	1.08	2.09	2.05
22	5.31	0.17	5.48	2.68	0.61	-	3.29	8.77	1.08	2.10	2.05
23	4.90	0.19	5.09	3.28	0.53	-	3.81	8.90	1.02	2.04	2.05
24	4.80	0.20	5.00	3.30	0.57	-	3.87	8.87	1.03	2.05	2.04
25	5.04	0.13	5.17	3.18	0.57	-	3.75	8.92	1.03	2.02	2.03
26	5.02	0.17	5.19	3.13	0.59	-	3.72	8.91	1.02	2.03	2.03
27	4.83	0.19	5.02	3.32	0.53	-	3.85	8.87	1.05	2.04	2.03
28	4.77	0.20	4.97	3.35	0.60	-	3.95	8.92	1.01	2.05	2.03
29	5.31	0.17	5.48	2.68	0.62	-	3.30	8.78	1.07	2.10	2.06
30	5.24	0.17	5.41	2.73	0.69	-	3.42	8.83	1.07	2.08	2.02
31	5.02	0.21	5.23	3.12	0.57	-	3.69	8.92	1.04	2.04	2.01
32	4.93	0.16	5.09	3.34	0.55	-	3.89	8.98	1.02	2.01	1.98
33	5.25	0.18	5.43	2.69	0.69	-	3.38	8.81	1.06	2.08	2.04
34	4.79	0.20	4.99	3.33	0.58	-	3.91	8.90	1.04	2.05	2.02
35	5.10	0.22	5.32	2.89	0.61	-	3.50	8.82	1.06	2.08	2.03
36	5.11	0.17	5.28	3.04	0.57	-	3.61	8.89	1.03	2.04	2.03
37	5.18	0.17	5.35	2.76	0.71	-	3.47	8.82	1.06	2.06	2.05
38	5.12	0.22	5.34	2.85	0.60	-	3.45	8.79	1.08	2.09	2.04
39	5.15	0.21	5.36	2.76	0.62	-	3.38	8.74	1.07	2.10	2.08
40	4.80	0.20	5.00	3.32	0.58	-	3.90	8.90	1.03	2.04	2.03

§ The analytical results (in wt.%) are listed in Table 7 (JEOL-8900 electron microprobe). These results are quoted in atoms per formula unit.

S 5.08 (4.83–5.37), and total 99.95, and the formula is $(Pd_{5.18}Pt_{0.15})_{\Sigma 5.33}(Cu_{2.12}Ag_{0.74}Fe_{0.61})_{\Sigma 3.47}Sn_{1.06}Te_{2.09}S_{2.04}$ (Σatoms = 14). In terms of *apfu*, the following variations are observed: Pd 4.82–5.40, Pt 0.11–0.27, Cu 1.46–3.23, Fe 0.55–0.71, Ag 0.03–1.41, Sn 1.01–1.10, Te 2.03–2.13, and S 1.99–2.09. The (Pd + Pt) value varies from 5.02 to 5.51, with a mean of 5.33 *apfu*, the (Cu + Fe + Ag) value varies from 3.27 to 3.83, with a mean of 3.48 *apfu*, and ΣMe ranges from 8.70 to 8.93, with a mean of 8.81 *apfu*. The concentrations of Cu and Ag display a near-perfect negative correlation: R = –0.99 (Fig. 10), indicative of the Ag-for-Cu substitution. The correlation between the values (Pd + Pt) and (Cu + Fe + Ag) also is strongly negative (R = –0.94: Fig. 11).

TABLE 9. CHEMICAL COMPOSITION§ OF Ag-RICH OULANKAITE FROM THE LUKKULAISVAARA INTRUSION, KARELIA, RUSSIA

	Pd	Pt	Cu	Fe	Ag	Sn	Te	S	Total
1	43.51	2.35	6.12	2.67	11.32	9.06	20.03	4.77	99.83
2	42.87	2.34	5.96	2.71	11.10	9.09	20.30	4.89	99.26
3	42.87	2.22	5.91	2.62	11.49	9.12	20.19	4.85	99.27
4	43.99	1.79	6.39	2.61	10.38	9.02	20.53	4.81	99.52
5	43.70	1.90	6.40	2.56	9.93	9.24	20.38	4.92	99.03
6	43.92	1.98	6.53	2.65	9.72	9.07	20.27	4.88	99.02
7	43.54	1.57	6.02	2.57	11.13	9.00	20.36	4.83	99.02
8	42.01	2.41	6.00	2.62	12.15	9.05	19.83	4.72	98.79
9	42.54	2.41	6.33	2.64	11.17	9.07	19.83	4.83	98.82
10	42.20	2.41	6.37	2.62	11.64	9.03	20.13	4.92	99.32
11	42.74	2.51	6.51	2.64	10.86	9.17	20.02	4.83	99.28
12	42.16	2.32	6.00	2.56	11.52	9.05	20.04	4.86	98.51
13	42.92	2.02	6.65	2.65	10.55	9.10	20.08	4.95	98.92
14	42.56	1.91	6.44	2.55	10.52	9.19	20.33	4.90	98.40
15	41.58	2.54	5.86	2.63	12.21	9.05	19.80	4.98	98.65
16	43.66	2.30	8.15	2.96	8.27	9.21	20.38	4.93	99.86
17	43.46	2.06	8.53	2.66	7.62	9.26	20.34	4.96	98.89
18	43.13	2.13	7.78	2.64	9.00	9.17	20.17	4.97	98.99
19	43.00	1.90	6.26	2.81	11.44	9.05	19.93	4.91	99.30
20	43.43	1.86	6.49	2.66	10.96	9.00	19.99	4.89	99.28
21	43.46	1.99	7.25	2.68	9.79	8.91	20.21	4.92	99.21
22	43.49	1.91	8.82	2.62	6.77	9.35	20.27	4.96	98.19
23	43.25	2.34	9.48	2.71	5.41	9.33	20.62	5.05	98.19
24	42.91	2.16	6.81	3.02	10.31	9.23	20.06	4.94	99.44
25	42.56	1.97	6.54	3.08	10.73	8.99	19.92	5.04	98.83
26	43.26	1.93	7.65	2.50	8.60	9.20	19.77	4.91	97.82
27	43.58	1.88	9.00	2.48	6.40	9.17	20.11	4.91	97.53
28	43.87	2.09	7.42	3.01	8.28	9.26	20.43	4.98	99.34
*29**	43.08	2.11	6.92	2.68	9.97	9.12	20.15	4.90	98.93

§ Cameca Camebax electron microprobe; results quoted in wt.%
* The average results of the analyses (1 to 28).

TABLE 10. ATOMIC PROPORTIONS§ (ΣATOMS = 14) OF ARGENTOAN OULANKAITE FROM THE LUKKULAISVAARA INTRUSION, KARELIA, RUSSIA

	Pd	Pt	ΣPd, Pt	Cu	Fe	Ag	ΣCu, Fe, Ag	Σ*Me*	Sn	Te	S
1	5.44	0.16	5.60	1.28	0.64	1.40	3.32	8.92	1.02	2.09	1.98
2	5.38	0.16	5.54	1.25	0.65	1.37	3.27	8.81	1.02	2.12	2.04
3	5.39	0.15	5.54	1.24	0.63	1.42	3.29	8.83	1.03	2.12	2.02
4	5.50	0.12	5.62	1.34	0.62	1.28	3.24	8.86	1.01	2.14	1.99
5	5.48	0.13	5.61	1.34	0.61	1.23	3.18	8.79	1.04	2.13	2.05
6	5.50	0.14	5.64	1.37	0.63	1.20	3.20	8.84	1.02	2.12	2.03
7	5.47	0.11	5.58	1.27	0.62	1.38	3.27	8.85	1.01	2.13	2.01
8	5.31	0.17	5.48	1.27	0.63	1.52	3.42	8.90	1.03	2.09	1.98
9	5.36	0.17	5.53	1.33	0.63	1.39	3.35	8.88	1.02	2.08	2.02
10	5.28	0.16	5.44	1.34	0.62	1.44	3.40	8.84	1.01	2.10	2.04
11	5.36	0.17	5.53	1.37	0.63	1.34	3.34	8.87	1.03	2.09	2.01
12	5.33	0.16	5.49	1.27	0.62	1.44	3.33	8.82	1.03	2.11	2.04
13	5.37	0.14	5.51	1.39	0.63	1.30	3.32	8.83	1.02	2.09	2.05
14	5.36	0.13	5.49	1.36	0.61	1.31	3.28	8.77	1.04	2.14	2.05
15	5.24	0.17	5.41	1.24	0.63	1.52	3.39	8.80	1.02	2.08	2.08
16	5.36	0.15	5.51	1.68	0.69	1.00	3.37	8.88	1.01	2.09	2.01
17	5.38	0.14	5.52	1.77	0.63	0.93	3.33	8.85	1.03	2.10	2.04
18	5.35	0.14	5.49	1.62	0.62	1.10	3.34	8.83	1.02	2.09	2.05
19	5.37	0.13	5.50	1.31	0.67	1.41	3.39	8.89	1.01	2.07	2.03
20	5.42	0.13	5.55	1.36	0.63	1.35	3.34	8.89	1.01	2.08	2.03
21	5.40	0.13	5.53	1.51	0.63	1.20	3.34	8.87	0.99	2.10	2.03
22	5.40	0.13	5.53	1.83	0.62	0.83	3.28	8.81	1.04	2.10	2.04
23	5.35	0.16	5.51	1.96	0.64	0.66	3.26	8.77	1.03	2.13	2.07
24	5.32	0.15	5.47	1.42	0.71	1.26	3.39	8.86	1.03	2.08	2.03
25	5.30	0.13	5.43	1.36	0.73	1.32	3.41	8.84	1.00	2.07	2.08
26	5.44	0.13	5.57	1.61	0.60	1.07	3.28	8.85	1.04	2.07	2.05
27	5.45	0.13	5.58	1.88	0.59	0.79	3.26	8.84	1.03	2.10	2.04
28	5.43	0.14	5.57	1.54	0.71	1.01	3.26	8.83	1.03	2.11	2.04
*29**	5.38	0.14	5.52	1.45	0.64	1.23	3.32	8.84	1.02	2.10	2.03

§ The analytical results (in wt.%) are listed in Table 9 (Cameca Camebax microprobe).
* The average results of the analyses (1 to 28). These results are quoted in atoms per formula unit.

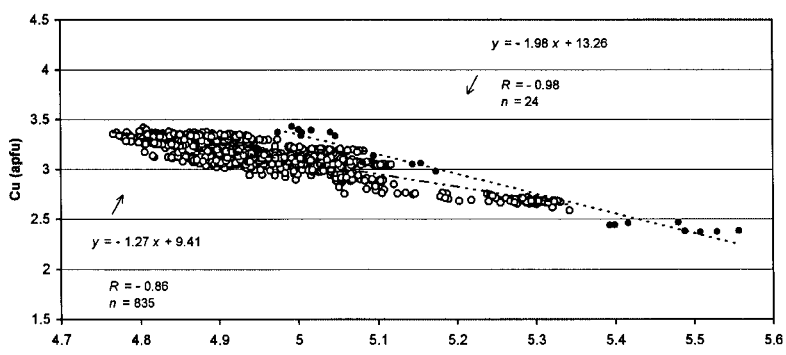


FIG. 9. Cu–Pd correlation (in *apfu*; Σatoms =14) in compositions of Ag-poor oulankaite from the Lukkulaisvaara intrusion. See Figure 8 for the key to the symbols.

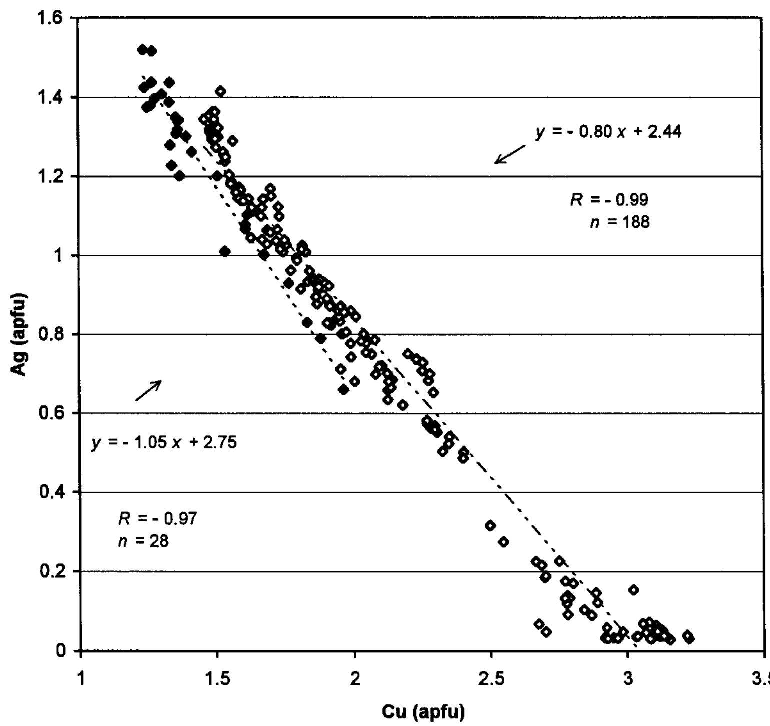


FIG. 10. Ag–Cu correlation (in *apfu*; Σatoms =14) in compositions of members of the argentoan oulankaite series from the Lukkulaisvaara intrusion. Results of one hundred and eighty-eight WDS analyses (JEOL–8900 electron microprobe: open diamonds) and twenty-eight WDS analyses (Cameca Camebax electron microprobe: filled diamonds) are plotted.

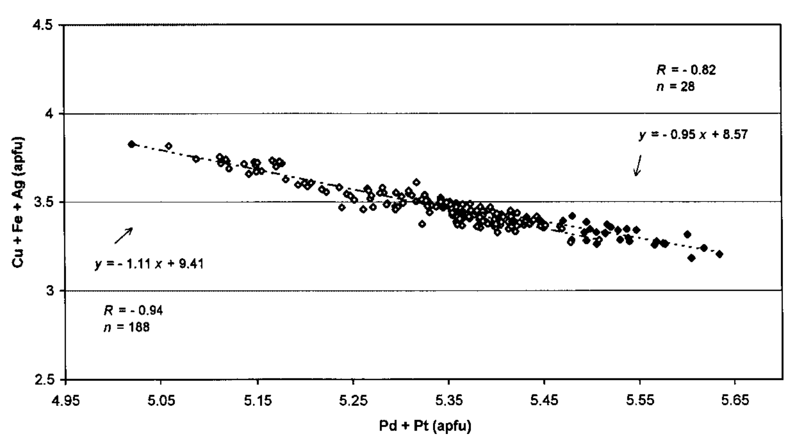


FIG. 11. Compositional variation of the argentoan oulankaite series in terms of the plot of (Cu + Fe + Ag) *versus* (Pd + Pt) (*apfu*, Σatoms =14). See Figure 10 for the key to the symbols.

Figures 10 and 11 compare the results of the two WDS datasets for argentoan oulankaite. Though the larger of these sets displays a greater variation of composition, these results are in general agreement. However, there is disagreement concerning element-correlation relationships of Pd and Ag in the argentoan oulankaite. Results of one of these datasets (n = 188: JEOL–8900 microprobe) suggest the existence of a positive correlation between Pd and Ag (R = 0.8). Such correlation would seem to suggest that the incorporation of Ag is controlled in part by Pd in the substitution of (Pd + Ag) for Cu. This possibility is not supported by the other dataset (WDS: Cameca Camebax microprobe; n = 28), however, and by the EDS data as well, which all indicate that there are no clear correlations between Pd and Ag in argentoan oulankaite.

Substitution mechanisms in Ag-poor oulankaite and argentoan oulankaite

A broad range of Pd-for-Cu (+Fe) substitution is characteristic of Ag-poor oulankaite (Figs. 8, 9). The compositions imply that Pd occurs at both the *Pd* and *Cu* sites of oulankaite: the *Pd* site is completely occupied by Pd (+Pt) (*i.e.*, 5 *apfu*), and excess Pd enters the *Cu* site.

We also conclude that two different mechanisms of substitution likely exist in argentoan oulankaite, and these operate independently of one another: an extensive substitution of Ag for Cu in the *Cu* site is combined with substitution of Pd for Cu + Ag (+Fe) (Figs. 10, 11). The existence of these two mechanisms of substitution agrees well with all of the datasets obtained here.

TABLE 11. CHEMICAL COMPOSITION[§] OF Ag-RICH OULANKAITE FROM THE LUKKULAISVAARA INTRUSION, KARELIA, RUSSIA

	Pd	Pt	Cu	Fe	Ag	Sn	Te	S	Total
1	42.64	1.77	7.30	2.69	10.84	9.42	20.14	4.90	99.70
2	41.77	2.36	7.19	2.68	10.92	9.61	20.20	4.87	99.60
3	42.06	2.03	7.22	2.66	11.13	9.50	20.08	4.88	99.56
4	42.12	2.19	7.41	2.87	11.68	9.45	19.89	4.90	100.51
5	42.06	2.24	7.18	2.70	10.61	9.56	20.30	4.91	99.56
6	42.68	2.42	7.26	2.71	10.43	9.62	20.22	4.84	100.18
7	42.21	2.33	7.38	2.68	10.33	9.61	20.36	4.91	99.81
8	42.24	2.28	7.39	2.72	10.10	9.68	20.15	4.89	99.45
9	43.23	1.75	7.52	2.72	9.90	9.67	20.19	4.92	99.90
10	42.71	1.82	7.53	2.83	9.72	9.53	20.29	4.93	99.36
11	42.81	1.75	7.49	2.77	9.65	9.49	20.01	4.97	98.94
12	43.64	1.61	7.70	2.69	9.46	9.66	20.30	4.98	100.04
13	42.47	1.97	7.80	2.56	9.34	9.57	20.31	5.00	99.02
14	42.94	1.93	8.09	2.57	9.23	9.70	20.27	4.97	99.70
15	42.65	1.88	8.36	2.53	9.00	9.62	20.33	4.88	99.25
16	42.92	1.90	7.86	2.59	9.17	9.68	20.09	4.92	99.13
17	43.92	1.74	7.92	2.75	8.62	9.56	20.30	4.98	99.79
18	43.11	1.62	8.13	2.70	8.42	9.41	20.51	4.94	98.84
19	42.93	1.85	8.44	2.67	8.39	9.60	20.76	5.04	99.68
20	42.94	1.88	8.78	2.61	8.25	9.77	20.69	5.11	100.03
21	43.25	2.01	8.70	2.66	8.01	9.78	20.68	5.14	100.23
22	42.79	1.99	9.08	2.63	7.77	9.80	20.62	5.00	99.68
23	43.00	1.92	9.31	2.65	7.39	9.71	20.46	5.06	99.50
24	43.11	1.88	9.42	2.66	7.27	9.70	20.60	5.18	99.82
25	42.99	1.88	9.56	2.66	7.16	9.83	20.54	5.11	99.73
26	43.82	1.68	9.40	2.72	6.93	9.74	20.80	5.05	100.15
27	43.43	1.86	9.72	2.65	6.74	9.78	20.65	5.15	99.98
28	43.53	1.85	9.79	2.68	6.49	9.81	20.66	5.08	99.89
29	42.90	1.91	10.14	2.67	6.23	9.82	20.70	5.02	99.39
30	43.16	2.00	10.54	2.67	5.90	10.00	20.68	5.18	100.13
31	42.68	2.32	10.51	2.56	5.70	9.86	20.64	5.06	99.33
32	43.26	2.24	10.65	2.91	5.62	9.87	20.65	5.18	100.38
33	43.40	2.21	10.88	2.89	5.25	9.89	20.70	5.18	100.40
34	43.43	2.36	11.33	2.83	4.93	9.88	20.59	5.14	100.49
35	42.98	2.32	11.42	2.82	4.71	9.85	20.69	5.13	99.92
36	43.50	2.33	11.75	2.76	4.44	9.94	20.74	5.11	100.57
37	42.62	4.17	12.34	2.43	2.65	9.69	21.02	5.06	99.98
38	42.94	2.56	13.89	2.51	1.94	10.03	21.19	5.24	100.30
39	43.29	2.67	14.01	2.54	1.02	10.05	21.29	5.25	100.12
40	41.93	3.69	15.11	2.64	0.42	9.97	21.17	5.26	100.19

[§] Results of electron-microprobe analyses (JEOL-8900).

TABLE 12. ATOMIC PROPORTIONS[§] (ΣATOMS = 14) OF ARGENTOAN OULANKAITE FROM THE LUKKULAISVAARA INTRUSION, KARELIA, RUSSIA

	Pd	Pt	ΣPd, Pt	Cu	Fe	Ag	ΣCu, Fe, Ag	Σ*Me*	Sn	Te	S
1	5.28	0.12	5.40	1.51	0.63	1.32	3.46	8.86	1.04	2.08	2.01
2	5.19	0.16	5.35	1.50	0.63	1.34	3.47	8.82	1.07	2.09	2.01
3	5.22	0.14	5.36	1.50	0.63	1.36	3.49	8.85	1.06	2.08	2.01
4	5.17	0.15	5.32	1.52	0.67	1.41	3.60	8.92	1.04	2.04	2.00
5	5.22	0.15	5.37	1.49	0.64	1.30	3.43	8.80	1.06	2.10	2.02
6	5.28	0.16	5.44	1.50	0.64	1.27	3.41	8.85	1.07	2.09	1.99
7	5.23	0.16	5.39	1.53	0.63	1.26	3.42	8.81	1.07	2.10	2.02
8	5.25	0.15	5.40	1.54	0.64	1.24	3.42	8.82	1.08	2.09	2.02
9	5.33	0.12	5.45	1.55	0.64	1.20	3.39	8.84	1.07	2.08	2.01
10	5.29	0.12	5.41	1.56	0.67	1.19	3.42	8.83	1.06	2.09	2.02
11	5.31	0.12	5.43	1.56	0.66	1.18	3.40	8.83	1.06	2.07	2.05
12	5.36	0.11	5.47	1.58	0.63	1.15	3.36	8.83	1.06	2.08	2.03
13	5.27	0.13	5.40	1.62	0.61	1.14	3.37	8.77	1.06	2.10	2.06
14	5.29	0.13	5.42	1.67	0.60	1.12	3.39	8.81	1.07	2.08	2.03
15	5.28	0.13	5.41	1.73	0.60	1.10	3.43	8.84	1.07	2.10	2.00
16	5.32	0.13	5.45	1.63	0.61	1.12	3.36	8.81	1.08	2.08	2.03
17	5.40	0.12	5.52	1.63	0.64	1.05	3.32	8.84	1.05	2.08	2.03
18	5.34	0.11	5.45	1.69	0.64	1.03	3.36	8.81	1.05	2.12	2.03
19	5.27	0.12	5.39	1.73	0.62	1.02	3.37	8.76	1.06	2.12	2.05
20	5.24	0.13	5.37	1.79	0.61	0.99	3.39	8.76	1.07	2.11	2.07
21	5.27	0.13	5.40	1.77	0.62	0.96	3.35	8.75	1.07	2.10	2.08
22	5.24	0.13	5.37	1.86	0.61	0.94	3.41	8.78	1.08	2.11	2.03
23	5.26	0.13	5.39	1.91	0.62	0.89	3.42	8.81	1.06	2.09	2.05
24	5.24	0.12	5.36	1.92	0.62	0.87	3.41	8.77	1.06	2.09	2.09
25	5.23	0.12	5.35	1.95	0.62	0.86	3.43	8.78	1.07	2.08	2.06
26	5.32	0.11	5.43	1.91	0.63	0.83	3.37	8.80	1.06	2.11	2.03
27	5.26	0.12	5.38	1.97	0.61	0.81	3.39	8.77	1.06	2.09	2.07
28	5.28	0.12	5.40	1.99	0.62	0.78	3.39	8.79	1.07	2.09	2.05
29	5.23	0.13	5.36	2.07	0.62	0.75	3.44	8.80	1.07	2.10	2.03
30	5.20	0.13	5.33	2.13	0.61	0.70	3.44	8.77	1.08	2.08	2.07
31	5.20	0.15	5.35	2.14	0.59	0.69	3.42	8.77	1.08	2.10	2.05
32	5.19	0.15	5.34	2.14	0.67	0.67	3.48	8.82	1.06	2.07	2.06
33	5.20	0.14	5.34	2.18	0.66	0.62	3.46	8.80	1.06	2.07	2.06
34	5.20	0.15	5.35	2.27	0.65	0.58	3.50	8.85	1.06	2.05	2.04
35	5.16	0.15	5.31	2.30	0.65	0.56	3.51	8.82	1.06	2.07	2.05
36	5.19	0.15	5.34	2.35	0.63	0.52	3.50	8.84	1.06	2.07	2.02
37	5.15	0.27	5.42	2.50	0.56	0.32	3.38	8.80	1.05	2.12	2.03
38	5.08	0.17	5.25	2.75	0.57	0.23	3.55	8.80	1.06	2.09	2.06
39	5.13	0.17	5.30	2.78	0.57	0.12	3.47	8.77	1.07	2.10	2.06
40	4.94	0.24	5.18	2.98	0.59	0.05	3.62	8.80	1.05	2.08	2.06

[§] The analytical results (in wt.%) are listed in Table 11 (JEOL-8900 electron microprobe). These results are quoted in atoms per formula unit.

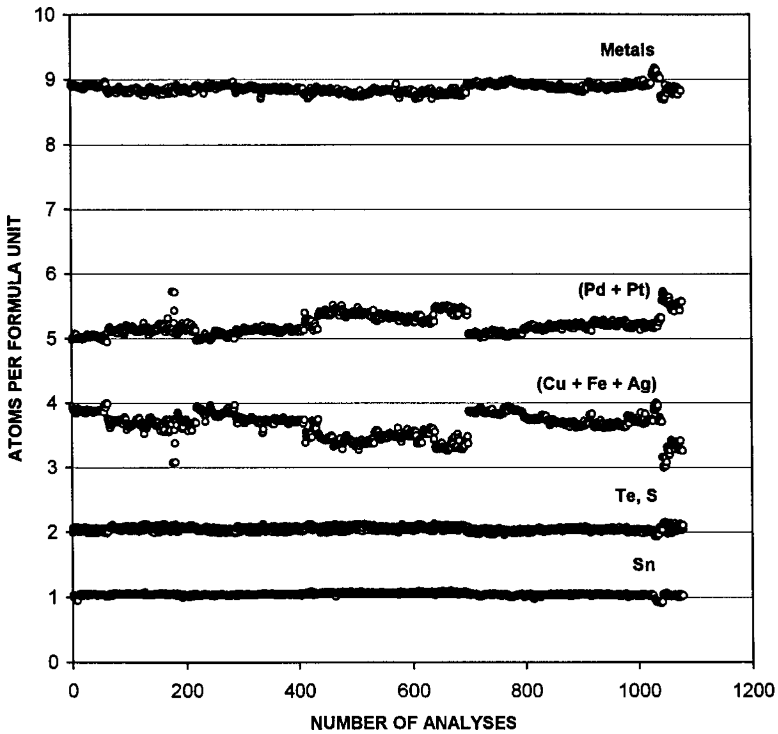


FIG. 12. Plot of values of atoms per formula unit: Sn, Te, S, (Cu + Fe + Ag), (Pd + Pt), and the total of metals, calculated on the basis of Σatoms = 14, *versus* the number of analyses. The numbers 1 – 1026 refer to results of WDS analyses done using the JEOL–8900 electron microprobe. The numbers 1027 – 1078 refer to results of WDS analyses done using the Cameca Camebax electron microprobe. The bulk of these compositions (1–1078) are free of Ag or are poor in Ag (<0.25 wt.% Ag). The compositions of argentoan oulankaite and Ag-dominant analogue of oulankaite are mostly plotted at the numbers 181–575 and 1051–1078.

Levels of Fe and Pt, total content of metals, and implications for a minor vacancy at the Cu site

In contrast to Ag, the incorporation of Fe in oulankaite and argentoan oulankaite appears to be limited (up to 3.8 wt.% Fe, *i.e.*, 0.85 Fe *apfu*). Also, there is no evidence that Pt can be a principal component of these minerals (≤4.3 wt.% Pt: 0.27 Pt *apfu*). However, uniform levels of these minor elements are invariably present, and could be a significant factor in the stabilization of the oulankaite solid-solution.

The Σ*Me* value appears to display a relationship with the Pd + Pt value. In Figure 12, we have summarized all the results of WDS analyses (*n* = 1078). They suggest that the Σ*Me* value is slightly lower in compositions richer in Pd + Pt, which are correspondingly poorer in (Cu + Fe + Ag). These Pd(+Pt)-rich compositions are thus slightly metal-deficient relative to the ideal value Σ*Me* = 9 *apfu*, and show a larger extent of deviation from this value (Fig. 12). In contrast, the compositions richer in (Cu + Fe + Ag) appear to be closer to the assumed ideal stoichiometry (9 metal *apfu*: Fig. 12). The results of the two different sets of WDS data are consistent with this relationship (Fig. 12), which is thus unlikely to be an artifact resulting from analytical problems. Thus, the minor vacancy at the *Cu* site could be related to the incorporation of the excess Pd at this site according to the following coupled substitution: $Pd^{2+} + \square = 2\ Cu^{+}$.

Levels of Sn, Te, and S, and generalized formulae of oulankaite and argentoan oulankaite

Contents of Sn, Te and S are virtually constant in oulankaite and argentoan oulankaite (Fig. 12), and they are in accord with the inferred ideal proportions. Some of our analytical data (EDS) imply that there is slight excess in Te (up to *ca.* 2.1 *apfu* Te) with respect to S, which is in turn slightly deficient; these variations are not supported by the bulk of the WDS analyses, however. In some cases, these minor deviations could be accounted for by analytical inaccuracy (EDS). The constant levels of Sn, Te and S observed in compositions of oulankaite and argentoan oulankaite (Tables 6, 8, 10, 12) imply that these elements occupy specific positions in the structure. In addition, the mutual presence of Sn and S is unusual for a PGM, although it is reported in unnamed PtSnS (*cf.* synthetic PtGeS with the structure of cobaltite: Entner & Parthé 1973) from the Bushveld complex, South Africa (Barkov *et al.* 2001).

The following formula for oulankaite and argentoan oulankaite (Pd, Pt)$_{5+x}$(Cu,Fe,Ag)$_{4-x}$SnTe$_2$S$_2$, with $0 \leq x < 1$, is based on the observed variations and deviations from the ideal stoichiometry (Figs. 12, 13). The generalized formula of the Ag-dominant analogue of oulankaite is (Pd, Pt)$_{5+x}$(Ag,Cu,Fe)$_{4-x}$SnTe$_2$S$_2$, with $0 \leq x < 1$.

Origin of the Ag enrichment in argentoan oulankaite

The reported series of argentoan oulankaite provides a new example of Ag-for-Cu substitution. Substitutions of this type are generally uncommon, presumably because of the large difference in atomic radius of Ag and Cu, although quite familiar in tetrahedrite (*e.g.*, Pattrick & Hall 1983). Wide ranges in the Ag-for-Cu substitution have been recently reported in the lenaite – chalcopyrite, acanthite – chalcocite (or argentite – digenite) and miargyrite – chalcostibite solid-solution series from near-surface Ag deposits (Samusikov & Gamyanin 1999). On the basis of textural characteristics, these authors concluded that the Ag-rich members of these compositional series precipitated at a late stage, commonly in the form of a rim on the Cu-rich members.

The Pd–Ag-rich pods at Lukkulaisvaara formed by crystallization of isolated volumes of H_2O-saturated melt, *in situ*, and Cl was an important component of fluid at a postmagmatic hydrothermal stage, at which most of the PGM, including the Pd–Ag tellurides and associated oulankaite, were deposited or redeposited (Barkov *et al.* 1999, 2001). These pods and stringers are notably enriched in both Pd and Ag; in this deposit, these elements are closely associated with each other to form widespread intergrowths of the Pd–(Pt)- and Ag-rich tellurides, which are associated with the Cl-rich ferropargasite (*e.g.*, Figs.1 to 5) and a Cl-dominant analogue of ferropargasite (up to 4.5 wt.% Cl). Occurrences of various tellurides of Pd, commonly in association with pegmatitic patches, are typical of many PGE deposits (*e.g.*, Stone *et al.* 1996).

The observed association of argentoan oulankaite with telargpalite and the Cl-rich ferropargasite is consistent with an environment of high activity of Ag and of volatiles (*e.g.*, Figs. 2, 3D, 6). Telargpalite, which is the main carrier of Ag in the pods and stringers, cuts almandine and thus probably formed at a temperature lower than temperatures of the garnet–hornblende and garnet–staurolite equilibria in this rock (~560 to 670ºC: Barkov *et al.* 1999, 2001). This suggestion is consistent with the replacement of moncheite by telargpalite, observed in the polymineralic intergrowths that contain the oulankaite (*e.g.*, Figs. 3A,C).

The argentoan oulankaite may be a primary PGM deposited from microvolumes of a late-stage liquid or fluid enriched in Pd, Ag, Cu, Sn, Te, and S at an advanced stage of postmagmatic crystallization. An alternative interpretation is that the argentoan oulankaite solid-solution is of secondary origin, formed as a result

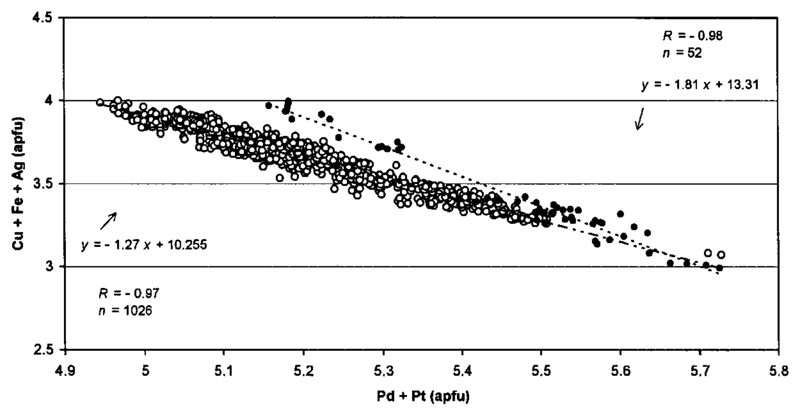


FIG. 13. Compositional variation of oulankaite and argentoan oulankaite in terms of the plot of (Cu + Fe + Ag) *versus* (Pd + Pt) (*apfu*, Σatoms = 14). Results of one thousand and twenty-six WDS analyses (JEOL–8900 electron microprobe: open circles) and fifty-two WDS analyses (Cameca Camebax electron microprobe: filled circles) are plotted.

of a subsolidus reaction involving a pre-existing oulankaite poor in Ag and a residual liquid or late-stage fluid enriched in Ag. Such an interpretation is corroborated by the heterogeneous distribution of Ag (5.4 to 12.2 wt.% Ag), observed in a grain of argentoan oulankaite (Fig. 3D).

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