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NEW Pd–Pb AND Pb–V OXIDES FROM A BONANZA-TYPE PGE-RICH, NEARLY BMS-FREE DEPOSIT IN THE PENIKAT LAYERED COMPLEX, FINLAND

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ABSTRACT

The Kirakkajuppura platinum-group-element (*PGE*) deposit, in the Penikat layered complex, Finland, is associated with the low-sulfide Sompujärvi *PGE* reef, located near the contact between ultramafic and gabbroic cumulates, close to the country rocks. The deposit is unique among *PGE* deposits in layered intrusions as it displays, on a relatively small scale, very high bulk-rock concentrations of *PGE* (up to ≥0.5 kg/t total *PGE*) along with a low content of S and Cr, *e.g.*, Σ*PGE* 224 ppm, 108 ppm S and 0.8 wt.% Cr; (Pd + Pt)/(Os + Ir + Ru) = 93.9 and Pd/Pt = 3.0 (mean of four whole-rock analyses). The platinum-group minerals (*PGM*), predominantly Pt–Ni-poor vysotskite–braggite, zvyagintsevite and a Pd–Pb oxide, mainly occur in altered pyroxenite, among grains of Mg-rich actinolite and clinochlore, as unusually large veinlet-like or chain-like aggregates up to ~1 cm in length. In agreement with the whole-rock data, the *PGM* do not show a close relationship with base-metal sulfides (*BMS*) and accessory chromite, occur in virtually *BMS*-free chromite-poor samples, and are mainly responsible for the bulk-rock S. Unnamed Pd_9PbO_{10} is the product of oxidation of the zvyagintsevite. It is anhydrous, is a very poor diffractor of X rays [the strongest two lines are 2.69(10vb) and 2.35(3) Å], and has a low reflectance (at 580 nm in air: R_1 20.2–20.7% and R_2 20.6–21.3%). Unnamed $Pb_4V_2O_9$ also occurs in the hydrous silicate association. The Kirakkajuppura *PGE* deposit cannot have formed as a result of the collection of the *PGE* by a magmatic sulfide liquid *in situ*. The late-stage *PGM*, responsible for the high *PGE* concentration in this deposit, precipitated from a hydrothermal fluids.

Keywords: platinum-group elements, platinum-group minerals, Pd–Pb oxide, Pb–V oxide, unnamed minerals, mafic-ultramafic rocks, Kirakkajuppura *PGE* deposit, Penikat complex, layered intrusion, Fennoscandian Shield, Finland.

SOMMAIRE

Le gisement de Kirakkajuppura, enrichi en éléments du groupe du platine (*EGP*), est situé dans le complexe stratiforme de Penikat, en Finlande. Il est associé au banc de Sompujärvi, à *EGP* et à faible teneur en sulfures, situé près du contact entre les cumulats ultramafiques et gabbroïques, tout près de l'interface avec les roches encaissantes. Le gisement est unique parmi les gisements de *EGP* des complexes stratiformes en atteignant, sur une échelle relativement restreinte, des teneurs extrêmement

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élevées en *EGP* dans les roches totales (jusqu'à ≥0.5 kg/t) et une faible teneur en S et Cr, *e.g.*, 224 ppm des *EGP*, 108 ppm de S et 0.8 wt.% de Cr; (Pd + Pt)/(Os + Ir + Ru) = 93.9 et Pd/Pt = 3.0 (moyenne de quatre analyses de roches totales). Les minéraux du groupe du platine (*MGP*), surtout vysotskite–braggite à faible teneur en Pt et en Ni, zvyagintsévite et un oxyde Pd–Pb, se trouvent surtout dans une pyroxénite altérée, parmi des grains d'actinolite magnésienne et de clinochlore, sous forme d'aggrégats en veinules ou en chaînes atteignant environ 1 cm en longueur. Tout comme l'indiquent les données obtenues sur roches totales, les *MGP* ne montrent pas de liens étroits avec les sulfures des métaux de base ou la chromite accessoire; ceux-ci se trouvent dans des roches essentiellement sans sulfures, et rendent donc compte de la teneur de ces roches en soufre. Un oxyde sans nom, de composition Pd_9PbO_{10}, serait le produit d'oxydation de la zvyagintsévite. Ce minéral est anhydre, et sa piètre cristallinité en fait un faible diffracteur de rayons X. Les deux raies les plus intenses du spectre de diffraction sont à 2.69 (intensité 10, très floue) et 2.35(3) Å. Il possède une faible réflectance (à 580 nm dans l'air: R_1 20.2–20.7% et R_2 20.6–21.3%). Un autre oxyde sans nom, $Pb_4V_2O_9$, est aussi associé aux silicates hydratés. Le gisement de Kirakkajuppura ne s'est pas formé par collection des *EGP* par un liquide magmatique sulfuré *in situ*. Plutôt, ces minéraux tardifs enrichis en éléments du groupe du platine auraient été précipités par voie hydrothermale.

(Traduit par la Rédaction)

Mots-clés: éléments du groupe du platine, minéraux du groupe du platine, oxyde de Pd–Pb, oxyde de Pb–V, minéraux sans nom, roches mafiques et ultramafiques, gisement de Kirakkajuppura, complexe de Penikat, massif intrusif stratiforme, bouclier fennoscandien, Finlande.

INTRODUCTION

Oxides of the platinum-group elements (*PGE*) rarely occur in nature. Clark *et al.* (1974) documented a Pd–(Hg)-bearing oxide at Itabira, Brazil, and suggested that it might be a mercurian variety of "palladinite" (not yet approved by the CNMMN, IMA), which was originally described from Brazil by Johnson and Lampadius as early as 1833 (Jedwab & Cassedanne 1998, and references therein). Davis *et al.* (1977) recorded a related Pd–Cu oxide at Itabira. Recently, "palladinite" (ideally PdO) has been rediscovered by Jedwab *et al.* (1993), and Olivo & Gauthier (1995) and Olivo *et al.* (1995) have reported related Cu–Fe-bearing PdO-type phases from Brazil. Various natural *PGE* oxides have been reported from a number of localities worldwide (Nixon *et al.* 1990, Weiser 1990, Augé & Legendre 1994, Jedwab 1995, Garuti *et al.* 1997, Krstić & Tarkian 1997).

We focus here on the occurrence and properties of an unnamed Pd–Pb oxide, which is the only natural Pb-rich *PGE* oxide so far known; it is a platinum-group mineral (*PGM*) of potential economic significance in the Kirakkajuppura *PGE* deposit, Penikat layered intrusion, Finland. We also present the characteristics of this unusual deposit, exceptionally enriched in *PGE* although it is nearly free of base-metal sulfides (*BMS*) and relatively poor in chromite. In addition, an unnamed Pb–V oxide is reported from this mineral deposit. The Pd–Pb oxide and associated minerals were studied both *in situ* and in heavy-mineral concentrates obtained from explosion dust.

GEOLOGICAL BACKGROUND

The geology, igneous stratigraphy, and mineralogy of the Penikat intrusion, one of the Early Proterozoic mafic–ultramafic layered complexes in the Fennoscandian Shield (Fig. 1), were described by Alapieti & Lahtinen (1986, 1989), Halkoaho *et al.* (1989a, b, 1990a, b), Huhtelin *et al.* (1989a, b, 1990), Halkoaho (1993) and Alapieti & Halkoaho (1995). The intrusion is about 23 km long and from 1.5 to 3.5 km wide (Fig. 2). The footwall rocks are mainly late Archean granitic rocks, and the wallrocks are younger tholeiitic flows, subvolcanic sills, and subordinate polymictic conglomerates. The intrusion is composed of five large blocks (namely Ala–Penikka, Keski–Penikka, Yli–Penikka, Kilkka and Sompujärvi) and shows characteristic features of layered intrusions, including the presence of marginal and layered series, and cryptic and megacyclic layering. The marginal series consists of a fine-grained chilled margin, which has a sharp contact with the footwall rocks, non-cumulate-textured gabbroic rocks, and some gabbronoritic and orthopyroxenitic cumulates. The layered series (*ca.* 2 km in total thickness) was divided into five megacyclic units (Alapieti & Lahtinen 1989, Halkoaho 1993), which are designated MCU I to MCU V. The MCU I unit is composed of orthopyroxene ± chromite orthocumulate, containing intercumulus plagioclase and augite; it is overlain by plagioclase–augite gabbroic cumulates. The MCU II and III units display quite similar geological structures; their lower parts are composed predominantly of layers of peridotitic and pyroxenitic rocks and chromite-dominant interlayers, whereas the upper parts are composed of plagioclase – augite – orthopyroxene cumulates of gabbroic affinity with some interlayers of plagioclase-bearing peridotite, websterite and anorthosite. The rocks of the upper part of the MCU III unit have a pegmatitic texture, and the MCU IV unit hosts the main *PGE* deposits (Fig. 2). The MCU IV unit consists of lower ultramafic olivine- and orthopyroxene-rich cumulates (about 20 m), which are overlain by gabbronoritic and anorthositic rocks about 1 km thick. The MCU V unit is composed of a lower layer of orthopyroxene cumulate (up to 7 m) and an overlying sequence of various

FIG. 1. Location of Early Proterozoic and Proterozoic mafic-ultramafic layered intrusions in the Fennoscandian Shield (based on various data from the literature).

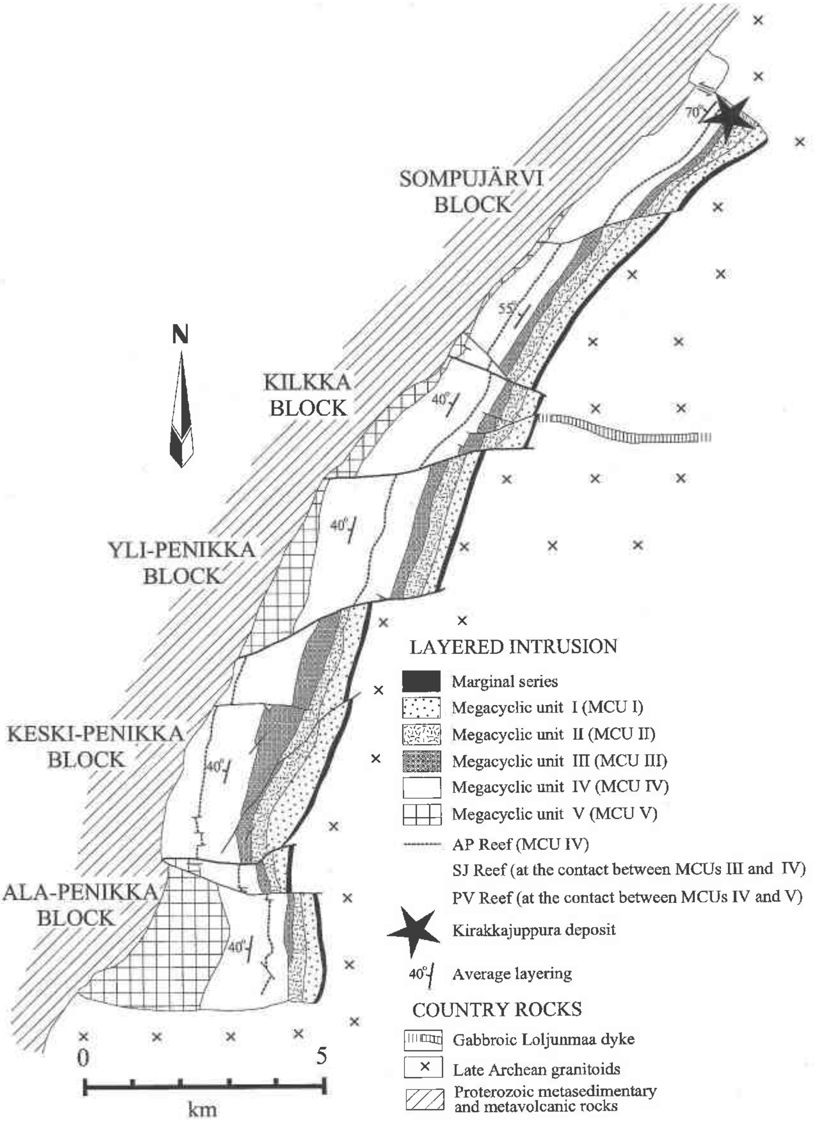

FIG. 2. Generalized geological map of the Penikat layered intrusion, Finland (Alapieti & Lahtinen 1986, Alapieti & Halkoaho 1995, and references therein), showing location of the Kirakkajuppura *PGE* deposit.

gabbroic rocks, which are plagioclase – orthopyroxene, plagioclase – orthopyroxene – clinopyroxene, and plagioclase – clinopyroxene cumulates.

Limited cryptic compositional variations are observed within the layered series (Halkoaho 1993); its upper contact is erosional, however, and the uppermost part of the section seems to have been removed (Alapieti & Lahtinen 1989). The olivine is completely altered in this complex. Ca-poor pyroxene varies from En_{81} at the lowermost stratigraphic level of the MCU I unit to En_{70} in the MCU V unit. Clinopyroxene varies within the ranges $Ca_{41.5–46.9}Mg_{41.6–50.5}Fe_{5.8–14.9}$, with the most magnesian augite found in the middle part of the MCU II unit. The cumulus plagioclase most strongly enriched in the anorthite end-member (An_{82}) is found in the middle MCU III unit. The intercumulus plagioclase

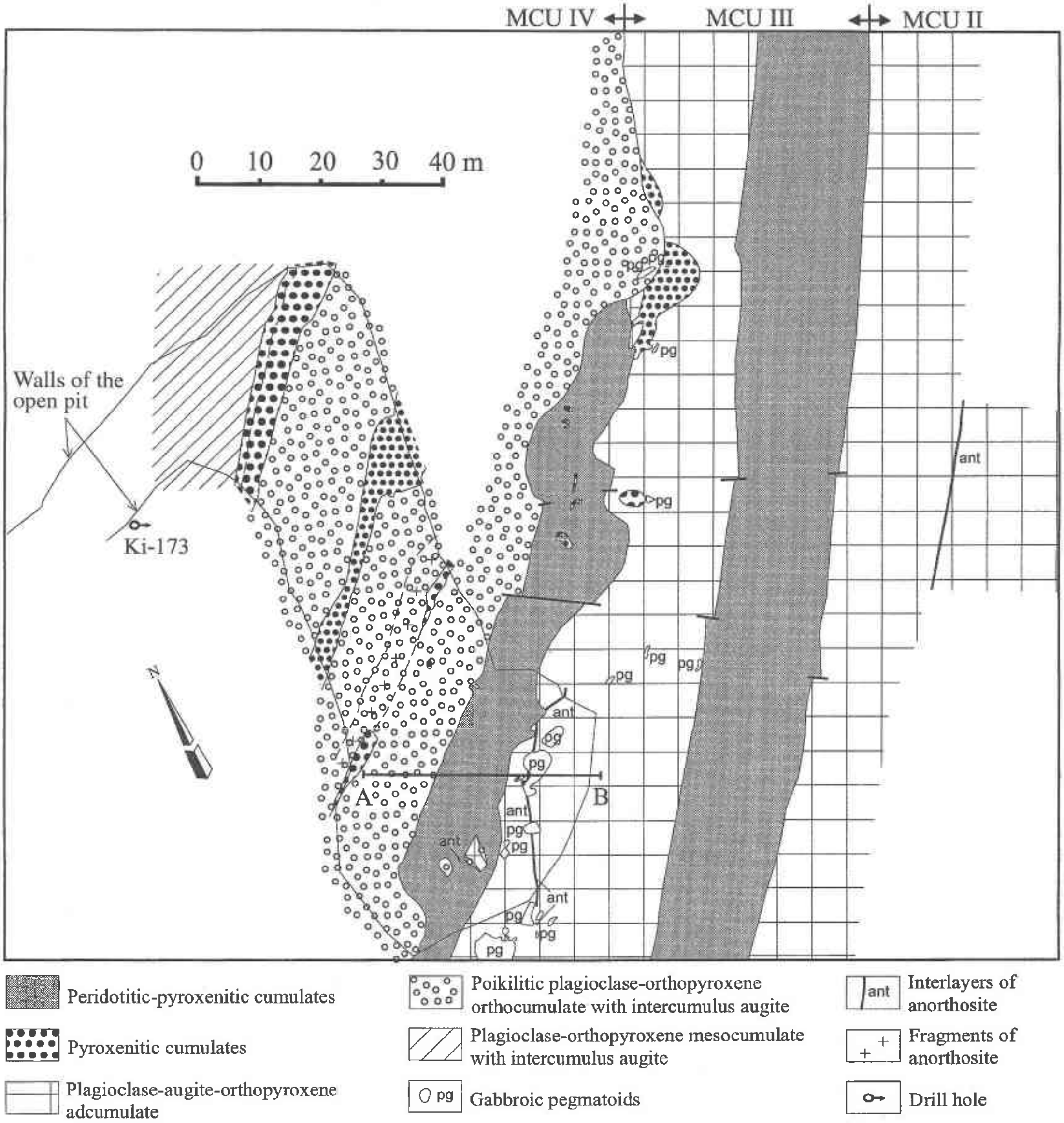

FIG. 3. Geological map of the Kirakkajuppura area, Penikat layered complex (Alapieti & Lahtinen 1989), showing the outline of an exploratory open pit.

from the lower MCU I unit and cumulus plagioclase from the MCU V unit are the poorest in anorthite (An_{56} and An_{60-61}, respectively).

THE KIRAKKAJUPPURA PGE DEPOSIT

Diverse assemblages of *PGM*, including the unnamed Pd–Pb oxide and the associated Pb–V oxide, occur in the Kirakkajuppura *PGE* deposit, at the northern end of the intrusion, relatively close to the country rocks (Fig. 2). The deposit is located at the contact between peridotitic–pyroxenitic and gabbroic cumulates (Figs. 3, 4), and is spatially associated with the low-sulfide Sompujärvi (SJ) *PGE* reef, which is situated at the boundary between the MCU III and MCU IV units (~0.5 to 1 km above the base of the complex) and extends along the entire length of the intrusion (Halkoaho 1993). Primary rock-forming minerals at Kirakkajuppura have been extensively replaced by hydrous silicates. Clinopyroxene (augite and diopside),

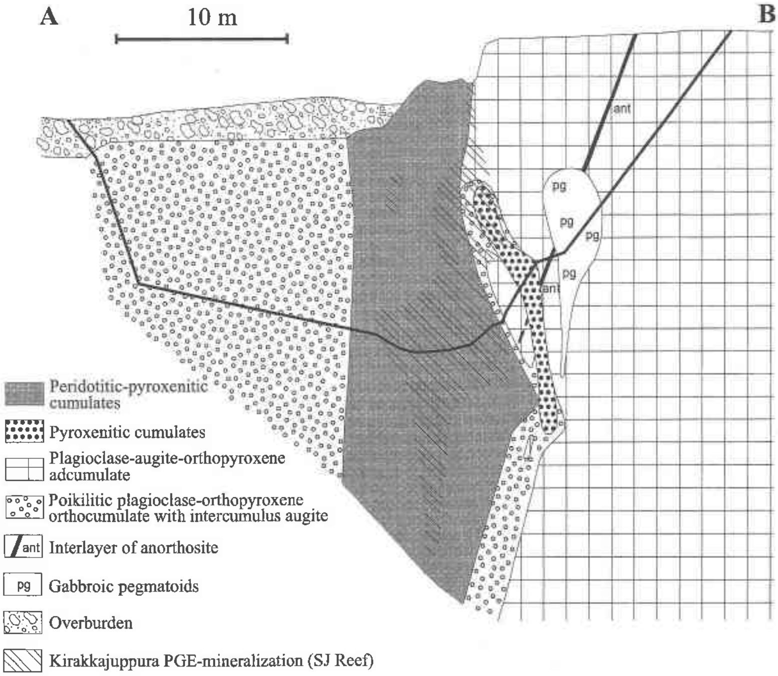

FIG. 4. Cross-section (A–B) through the *PGE*-mineralized zone, showing the main geological features of the Kirakkajuppura *PGE* deposit (see Fig. 3 for location and references). The outline of the exploratory open pit is drawn in bold.

TABLE 1. REPRESENTATIVE COMPOSITIONS OF HYDROUS SILICATES FROM THE KIRAKKAJUPPURA PGE DEPOSIT, PENIKAT COMPLEX, FINLAND

	Amphibole						Chlorite
SiO_2 wt.%	57.15	57.47	56.88	56.41	57.31	56.58	29.74
TiO_2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.07
Al_2O_3	0.21	0.25	0.59	0.63	0.17	0.38	16.85
Cr_2O_3	n.d.	n.d.	n.d.	n.d.	0.05	0.25	n.a.
FeO	9.30	8.07	8.82	8.18	7.12	7.19	17.55
MnO	0.13	0.18	0.12	0.19	0.23	0.25	0.12
MgO	19.24	19.70	19.15	19.42	19.32	19.52	24.06
NiO	n.a.	n.a.	0.17	n.d.	0.17	0.22	0.21
CaO	12.79	12.68	12.42	12.76	12.44	12.40	0.07
H_2O	2.15	2.15	2.14	2.13	2.13	2.12	11.95
Total	100.97	100.50	100.29	99.72	98.94	98.91	100.62
Si *apfu*	7.97	8.00	7.97	7.93	8.07	8.00	2.97
^{IV}Al	0.03	-	0.03	0.07	-	-	1.03
^{VI}Al	<0.01	0.04	0.07	0.04	0.03	0.06	0.96
Cr	-	-	-	-	<0.01	0.03	-
Fe	1.08	0.94	1.03	0.96	0.84	0.85	1.47
Mn	0.02	0.02	0.01	0.02	0.03	0.03	0.01
Mg	4.00	4.09	4.00	4.07	4.06	4.11	3.59
Ca	1.91	1.89	1.87	1.92	1.92	1.88	<0.01
Mg#	78.4	81.0	79.4	80.6	82.4	82.4	70.8

The wavelength-dispersion electron-microprobe analyses were carried out using a JEOL-733 instrument. All Fe as FeO; K, Na, Cl, and F were sought, but not detected. n.a.: not analyzed, n.d.: not detected. H_2O (wt.%) calculated from charge balance. Formulae calculated on the basis of $\Sigma(O + OH) = 24$ for amphibole and $\Sigma(O + OH) = 18$ for chlorite. Mg# = 100Mg/(Mg + Fe + Mn).

preserved in rocks in the vicinity of the ore deposit, exhibits significant compositional variations $Wo_{36.1-47.2}En_{40.1-49.9}Fs_{9.7-14.3}$. Accessory chromite, rich in Cr (34.0–43.3 wt.% Cr_2O_3) and in Al (11.3–16.2 wt.% Al_2O_3), strongly varies in terms of its 100Mg/(Mg + Fe^{2+}) and 100Fe^{3+}/(Fe^{3+} + Al + Cr) values, 3–30 and 5–22, respectively, and mostly plots within the compositional field of spinel from stratiform intrusions (Irvine 1967).

The accessory ilmenite is strongly enriched in Mn (3.4–11.1 wt.% MnO; *i.e.*, 7.5–25.3 mol.% pyrophanite end-member), and differs from most examples of ilmenite in layered intrusions, which, with a few exceptions, contain less than 1 wt.% MnO. The apatite analyzed is poor in Cl (<0.4 wt.% Cl) and rich in F (>2 wt.% F), and the mica (phlogopite) is relatively rich in Mg (Mg# 60.9–72.4; Mg# = 100Mg/(Mg + Fe + Mn), and does not contain detectable Cl.

The principal *PGE* mineralization at Kirakkajuppura is erratically distributed in a completely altered pyroxenite, which now consists predominantly of calcic amphibole (≥70 modal %), subordinate chlorite (clinochlore), and various amounts (≤10 modal %) of disseminated chromite, which is heterogeneously distributed in the rock. The *PGE*-mineralized zone is not, however, restricted to the pyroxenite; it extends to the adjacent gabbroic and peridotitic rocks (Fig. 4). In the

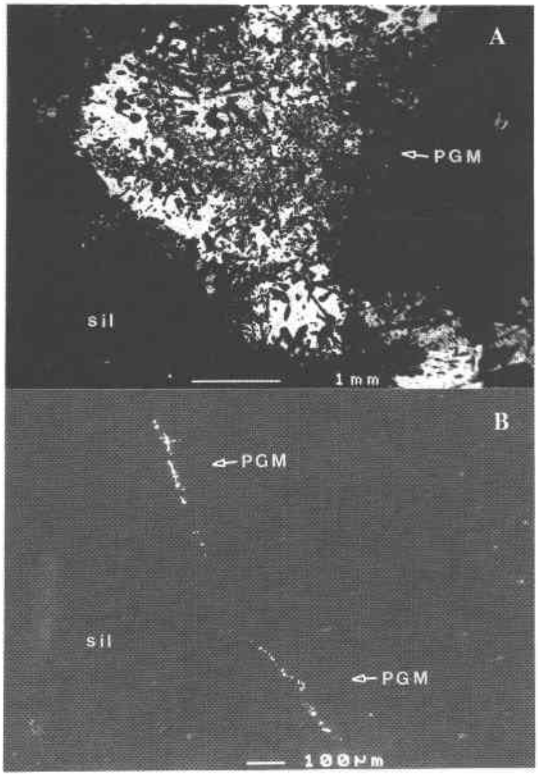

FIG. 5. Unusually large aggregates (A) and a chain-like veinlet (B) of platinum-group minerals (PGM), predominantly vysotskite – Pt-poor braggite (altered to various extent) and zvyagintsevite, among hydrous silicates (sil). Kirakkajuppura *PGE* deposit. Back-scattered electron (BSE) images. Scale bars: 1 mm (A) and 100 μm (B).

PGE-rich altered pyroxenite, both the amphibole (actinolite) and chlorite are Mg-rich (Mg# 80 and ≥70, respectively; Table 1), indicating a relatively high-magnesium precursor, the relict textures of which imply a coarse to pegmatitic grain-size prior to alteration.

The PGE mineralization

In terms of petrography, the *PGE*-rich pyroxenite is quite similar to altered mafic-ultramafic rocks in other layered intrusions. It can virtually be devoid of *BMS*. Cut specimens as large as ~10 cm may not contain any recognizable *BMS* but, instead, contain unusually large (up to ~1 cm in the longest dimension), megascopically visible aggregates of *PGM* among the hydrous silicates. The *PGM* aggregates are typically veinlet-like and are heterogeneously distributed in the rock. The *PGM* do not show a close relationship with accessory chromite. For instance, unusually large aggregates of *PGM* (Fig. 5A) are found in a polished section (~3 × 2.5 cm in size) virtually devoid of both *BMS* and chromite. In agreement with this observation, the maximum concentrations of *PGE* in the ore deposit were documented in a S–Cr-poor sample (250 and 9840 ppm of S and Cr, respectively). However, trace to accessory *BMS* are present in the rock, as chalcopyrite, bornite, millerite, and secondary chalcocite (grains ≤0.3 mm) are occasionally encountered in the concentrates of *PGE*-bearing minerals. Similarly, a chalcopyrite – bornite – millerite assemblage is associated with various *PGM* in *PGE*-rich mafic rocks of the neighboring layered intrusion, one of the layered intrusive bodies of the Oulanka complex (Fig. 1); these rocks are, in contrast, rich in *BMS* (Barkov *et al.* 1996).

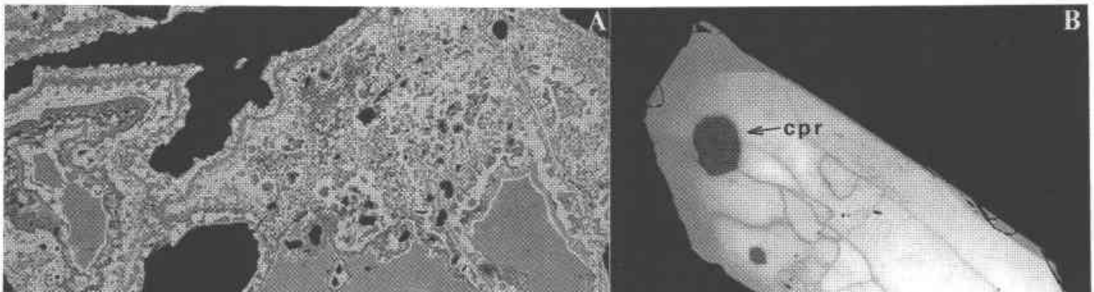

FIG. 6. Typical grains of vysotskite – braggite at Kirakkajuppura. A. Anhedral braggite, bg ($Pd_{0.78}Pt_{0.19}Ni_{0.05}S_{0.98}$), a part of *PGM* aggregates in Figure 5A, which is associated with Mg-rich calcic amphibole (am) and is replaced by very fine-grained aggregate of zvyagintsevite-related phases (white). B. Subhedral braggite, bg ($Pd_{0.77}Pt_{0.23}Ni_{0.02}S_{0.98}$; center of grain) with inclusions of Fe-rich cuprorhodsite, cpr [$(Cu_{0.65}Fe_{0.36})_{\Sigma 1.01}(Rh_{1.81}Ir_{0.12}Pt_{0.07}Co_{0.02})_{\Sigma 2.02}S_{3.97}$]. Black: epoxy. BSE images. Scale bars are 10 μm in each case.

TABLE 2. PLATINUM-GROUP MINERALS IN THE KIRAKKAJUPPURA PGE DEPOSIT

	main	subordinate	rare
Vysotskite-braggite	⊡		
Zvyagintsevite	⊡		
Pd–Pb oxide(s)	⊡		
Cuprorhodsite–malanite		⊡	
Laurite–erlichmanite		⊡	
Irarsite			⊡
Keithconnite			⊡
Pd-rich konderite			⊡
Palladian gold*			⊡
$Rh(Ni,Fe,Cu)_2S_3$			⊡
$(Fe_{0.5}Cu_{0.5})Rh_2S_4$**			⊡
$Pd_3Pb_2S_2$			⊡
(Pd,Pt)Cu			⊡

* Up to 9 wt.% Pd (WDS electron-microprobe data).
** Ferrorhodsite – cuprorhodsite – (malanite) series (see Barkov *et al.* 2000).

TABLE 3. REPRESENTATIVE WHOLE-ROCK COMPOSITIONS OF PGE-RICH, S-POOR ALTERED PYROXENITES FROM THE KIRAKKAJUPPURA PGE DEPOSIT, PENIKAT LAYERED COMPLEX, FINLAND

No.	1	2	3	4
SiO_2 wt.%	46.03	39.69	51.04	41.96
TiO_2	0.22	0.08	0.26	0.19
Al_2O_3	7.44	11.96	3.76	6.20
FeO	11.35	10.85	8.39	12.34
MnO	0.21	0.14	0.19	0.25
MgO	20.12	24.59	21.95	19.41
CaO	8.40	4.50	9.80	7.54
Na_2O	0.03	0.01	n.d.	0.02
K_2O	0.01	<0.01	<0.01	<0.01
Cr_2O_3	0.45	0.04	0.18	4.62
P_2O_5	0.03	n.d.	0.03	0.01
Total	94.28	91.86	95.61	92.54

No.	5	6	7	8	Average
Cr (ppm)	2060	3300	26900	1120	8345
Ni	500	760	850	580	673
Cu	10	10	100	250	93
S	60	70	160	140	108
Os (ppb)	122	610	780	94	401.5
Ir	420	1900	2600	330	1312.5
Ru	196	1020	1000	120	584
Rh	2300	7400	11200	1770	5667.5
Pt	21100	60600	116000	17100	53700
Pd	54700	203000	334000	56700	162100
Au	600	1340	1170	530	910
ΣPGE (ppm)	78.8	274.5	465.6	76.1	223.8
Pd/Pt	2.59	3.35	2.88	3.32	3.02
Pd/Ir	130.2	106.8	128.5	171.8	123.5
(Pt + Pd)/(Os + Ir + Ru)	102.7	74.7	102.7	135.7	93.9
Cu/Ni	0.02	0.01	0.12	0.43	0.14

Numbers 1–4 and 5–8 refer to different samples from the Kirakkajuppura deposit; however, samples 1 to 4 contain approximately the same level of *PGE* as samples 5–8. ppm: parts per million; ppb: parts per billion. Results for samples 5–8 are selected from those reported by Halkoaho *et al.* (1989a).

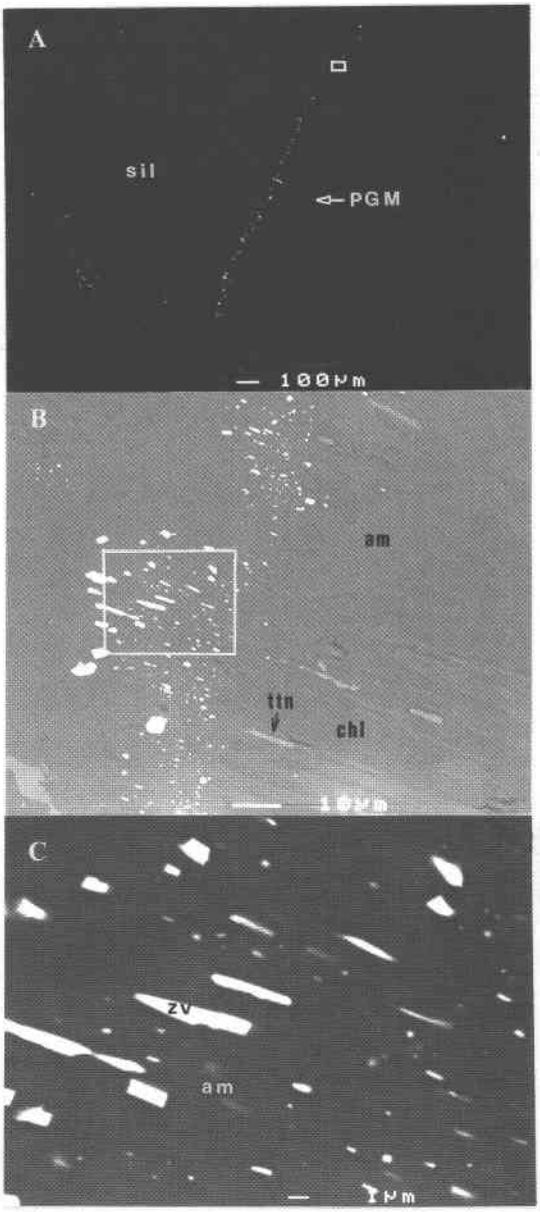

FIG. 7. A. Chain-like veinlet of zvyagintsevite and minor vysotskite – braggite, Pd–(Cu–Fe–Pt)–Pb oxide, and keithconnite (PGM) among hydrous silicates (sil). B. Magnification of part of the veinlet (outlined in Fig. 7A), showing numerous, minute crystals of zvyagintsevite (white) within Mg-rich calcic amphibole (am; actinolite) and chlorite (chl; clinochlore); ttn: secondary titanite. Note subparallel orientation of the zvyagintsevite, titanite and amphibole. C. Further magnification of area shown in Figure 7B. Note subparallel orientation of the zvyagintsevite (zv, white), including the grains less than 0.5 μm in size; am: host amphibole. BSE images. Scale bars: 100 μm (A), 10 μm (B) and 1 μm (C).

Pt-poor members of the vysotskite – braggite series, zvyagintsevite, and the Pd–Pb oxide are the main *PGM* at Kirakkajuppura. The large aggregates of *PGM* are composed mainly of vysotskite – braggite, which is altered and probably oxidized to various degrees, and commonly replaced by very fine-grained aggregates of zvyagintsevite and related secondary Pd–(Pt–Cu)–Pb-rich *PGM* (Fig. 6A). Such unusually large grains of braggite (8 mm) were previously reported from the Stillwater complex (Criddle & Stanley 1985). Braggite also occurs as subhedral grains, which may display abundant fractures and late alteration along these fractures (Fig. 6B). There are also thiospinel *PGM* (malanite – cuprorhodsite – ferrorhodsite series) in these aggregates. Various *PGM*, identified in the mineral deposit, are listed in Table 2; a more detailed description will be given separately.

Bulk-rock compositions (Table 3) are consistent with mineralogical observations, indicating that, in general, the Pd–Pt sulfides predominate over all other *PGM* in the deposit. Owing to this predominance, bulk-rock concentrations of Pd, Pt and S (atom %) in the *BMS*-free or very-low- sulfide samples (*e.g.*, no. 6 and 7, Table 3) give atomic proportions of vysotskite – braggite; it should be noted that, unlike other localities, Ni is not essential in the Kirakkajuppura vysotskite – braggite. For instance, bulk-rock composition number 6 (Pd 203, Pt 60.6, and S 70 ppm) yields a nearly ideal braggite-type formula $(Pd_{0.87}Pt_{0.14})_{\Sigma 1.01}S_{0.99}$ (basis: Σ atoms = 2), and number 7 gives a similar chemical formula $(Pd_{0.72}Pt_{0.14})_{\Sigma 0.86}S_{1.14}$. Some of the *PGE*-rich samples exhibit an excess of S relative to vysotskite – braggite stoichiometry, indicating that other sulfides (trace *BMS*) also are present in the rock.

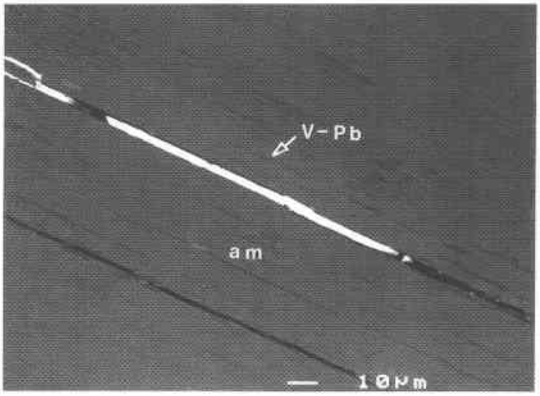

FIG. 8. Unnamed Pb–V oxide (V–Pb) filling cleavage in Mg-rich calcic amphibole, am (actinolite). BSE image. Scale bar: 10 µm.

The presence of unusual chain-like veinlets of *PGM*, which cut the hydrous silicates (*e.g.*, Figs. 5B, 7A), is a remarkable feature. These veinlets are up to ~1 mm in length, and the number of *PGM* grains in such chains exceeds 300, whereas the individual grains are, in general, very small (<1 to 50 µm; mainly ≤10 µm). Within a chain (Fig. 7A), a subparallel orientation of microcrystalline *PGM*, hydrous silicates and secondary titanite is locally observed (Fig. 7B). This textural relationship suggests that deposition of these late-stage *PGM* was controlled by both fractures and cleavages in the hydrous silicates. Scanning electron microscopy (SEM), coupled with quantitative energy-dispersion spectrometry (EDS, finely focused beam, 100-s count periods, and Link ISIS revision 3.2 program) were applied to characterize the components of the chains. They are principally composed of zvyagintsevite, subordinate vysotskite – (Pt-poor) braggite, Pd–(Pt–Cu–Fe)–Pb oxide, and a very rare Pd-rich telluride, probably keithconnite, $Pd_{20.14}(Te_{6.52}Bi_{0.34})_{\Sigma 6.86}$ (basis: Σ atoms = 27). Interestingly, the chain shown in Figure 7A is nearly monomineralic, and includes numerous submicroscopic, mostly subhedral to euhedral crystals of zvyagintsevite. The SEM–EDS technique allowed us to analyze grains as small as ≤1 µm, and acceptable totals (100 ± 2 wt.%) were obtained. EDS analyses of selected grains of zvyagintsevite (*n* = 34) were carried out throughout this chain (Fig. 7A) and gave the following mean (with ranges): Pd 58.75 (57.5–60.0), Pt 1.15 (0.7–1.6), Pb 40.10 (38.9–41.0), Sn not detected (0.0–0.6), total (not normalized) of 100.0 wt. % (98.0–101.8), corresponding to $(Pd_{2.94}Pt_{0.03})_{\Sigma 2.97}Pb_{1.03}$. In addition, about twenty subparallel grains of zvyagintsevite, less than 0.8 µm in size (Fig. 7C), were analyzed semiquantitatively with the EDS and their (Pd + Pt)/(Pb + Sn) value is close to 3. Results of wavelength-dispersion (WDS) electron-microprobe analyses are in good agreement with the EDS results, and indicate that, unlike the type occurrence at Noril'sk (Genkin *et al.* 1966), the zvyagintsevite at Kirakkajuppura is poor in Pt and Sn, and is close to end-member Pd_3Pb. Electron-microprobe analyses (EDS and WDS; *n* = 18) of the vysotskite –

TABLE 4. CHEMICAL COMPOSITION[§] OF UNNAMED Pb–V OXIDE* FROM THE PENIKAT LAYERED COMPLEX, FINLAND

No.	1	2	3	4	5
PbO wt.%	83.31	84.12	84.25	83.51	84.25
V_2O_5	16.16	16.39	16.19	16.16	16.57
Total	99.47	100.51	100.44	99.67	100.82
			Atomic proportions (O = 9)		
Pb *apfu*	4.11	4.10	4.13	4.12	4.08
V	1.96	1.96	1.95	1.95	1.97

[§] Quantitative EDS-SEM electron-microprobe analyses. Cu, Ni, Co, Mn, Ti, and Cr were sought, but not detected. As a test, this Pb–V oxide also was analyzed for Si. Low content of Si in these results (0.4-0.5 wt.% SiO_2; excluded from the total) indicates very minor contamination by the host (actinolite). *apfu*: atoms per formula unit. * Veinlet shown in Figure 8.

braggite in different textural associations yield 13–37, mean ~20 mol.% PtS. These compositions agree with those derived from the bulk-rock analyses (14–25 mol. % PtS).

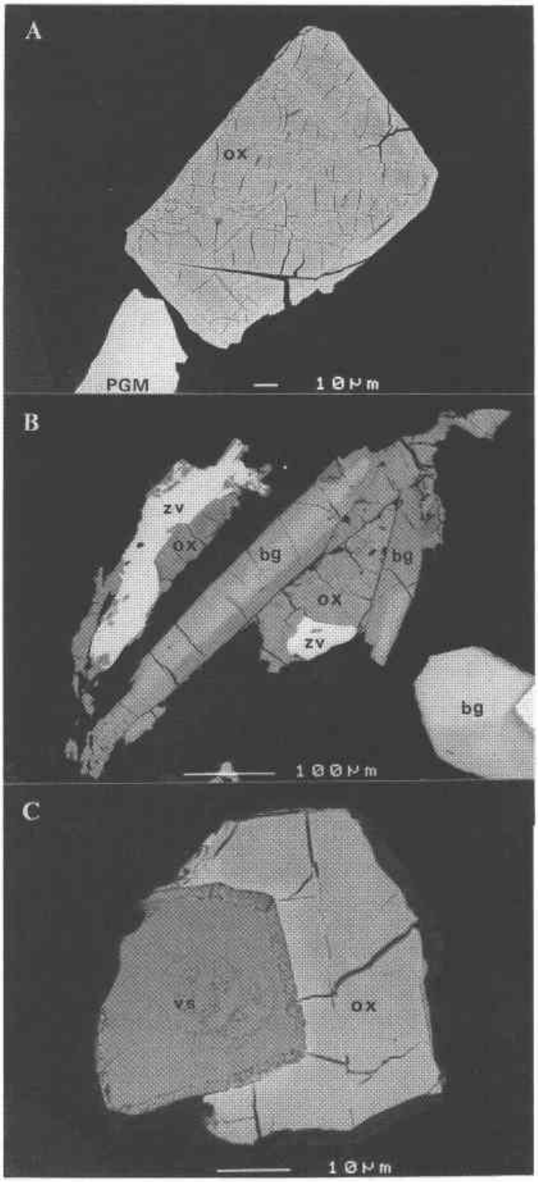

FIG. 9. Grains of the unnamed Pd–Pb oxide, ox (mounted in epoxy, black), associated with zvyagintsevite (zv), Pt-poor braggite (bg) and vysotskite (vs). Note the subhedral (presumably pseudomorphous) outlines of the oxide, its fractured appearance (A), clear replacement relations with zvyagintsevite (B), and intergrowth relationships with nearly end-member vysotskite, $Pd_{1.00}Ni_{0.02}Pt_{<0.01}S_{0.97}$ (C). BSE images. Scale bars: 10 µm (A and C), and 100 µm (B).

UNNAMED LEAD–VANADIUM OXIDE

An unusual Pb–V-rich phase (Fig. 8) was identified in spatial association with the late-stage *PGM* and hydrous silicates. It fills a cleavage in a Mg-rich calcic amphibole (actinolite; Mg# 80.4). As in the case of the microcrystalline zvyagintsevite (Fig. 7), it is a very late phase, whose deposition was controlled by the actinolite's cleavage. Examination under SEM–EDS reveals V, Pb and O as the constituents. EDS analyses of the phase (Table 4) were carried out using pure metal standards (and SiO_2 for Si) and a finely focused beam (~1 µm). A low content of Si (0.4–0.5 wt.% SiO_2) encountered in these analyses indicates very minor contamination by the host (actinolite). The electron-microprobe results indicate that the phase differs in composition from chervetite (the only Pb–V oxide mineral known: $Pb_2V_2O_7$; Bariand *et al.* 1963) and appears to represent a new mineral. The ideal formula, suggested by the analytical results, is $Pb_4V_2O_9$ and requires Pb^{2+} and V^{5+} in order to maintain charge balance. This Pb–V oxide may be a natural equivalent of synthetic $Pb_4V_2O_9$ (PDF 26–1163), but its small grain-size precludes a more detailed examination.

UNNAMED PALLADIUM–LEAD OXIDE

Appearance

The Pd–Pb oxide occurs as both subhedral and anhedral grains (up to 0.2–0.3 mm), which typically display abundant fractures (like syneresis cracks; Fig. 9A). An alteration along late linear fractures also is observed. Textural evidence suggests that the oxide is a replacement product of zvyagintsevite (Fig. 9B), imply-

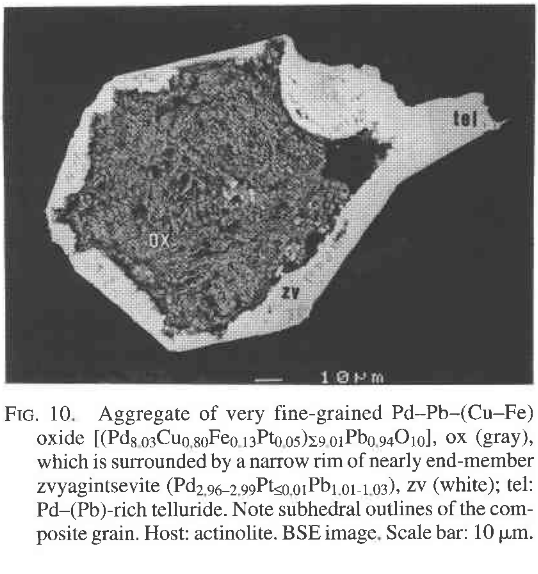

FIG. 10. Aggregate of very fine-grained Pd–Pb–(Cu–Fe) oxide $[(Pd_{8.03}Cu_{0.80}Fe_{0.13}Pt_{0.05})_{\Sigma 9.01}Pb_{0.94}O_{10}]$, ox (gray), which is surrounded by a narrow rim of nearly end-member zvyagintsevite ($Pd_{2.96–2.99}Pt_{\leq 0.01}Pb_{1.01-1.03}$), zv (white); tel: Pd–(Pb)-rich telluride. Note subhedral outlines of the composite grain. Host: actinolite. BSE image. Scale bar: 10 µm.

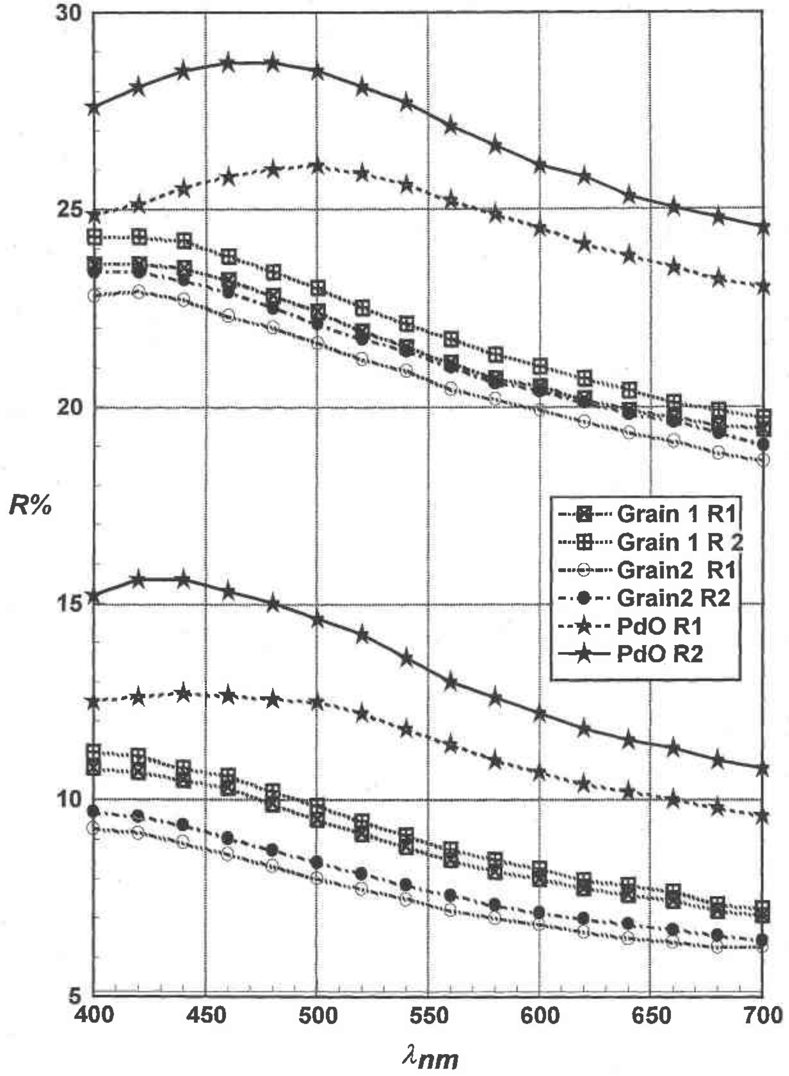

FIG. 11. Reflectance spectra for two grains of the unnamed Pd–Pb oxide from Penikat, grains 1 and 2, both measured in air and in oil, compared with the spectra for "palladinite" [$(Pd_{0.93}Cu_{0.06}Hg_{0.005}Fe_{0.003})_{\Sigma 1.00}O$; basis: O = 1] from the type locality, Itabira, Brazil (Jedwab *et al.*, unpubl. data).

ing that the subhedral habit is pseudomorphous. Oxide grains may contain relics of zvyagintsevite and also vysotskite – braggite crystal(s); the latter have remained well preserved during a selective replacement of zvyagintsevite by the oxide. The oxide grains are commonly heterogeneous. Single, rather homogeneous grains also are present, however (*e.g.*, Fig. 9A), but X-ray powder-diffraction indicates that they are cryptocrystalline. The oxide is found partly mantling vysotskite (Fig. 9C); it may well have formed at the expense of pre-existing zvyagintsevite, rather than the vysotskite, however.

Figure 10 shows some unusual textural relationships involving the Pd–Pb oxide. Very fine-grained Pd–(Cu,Fe)–Pb oxide is surrounded by a thin rim of zvyagintsevite. The outline of this composite grain indicates its subhedral habit before alteration. Two different interpretations can be proposed. The first is that the rim represents relics of a pre-existing subhedral grain of zvyagintsevite. Owing to a particular feature (*e.g.*,

TABLE 5. REFLECTANCE DATA FOR TWO GRAINS OF UNNAMED Pd–Pb OXIDE FROM THE PENIKAT LAYERED COMPLEX, FINLAND

λ, nm	Grain 1 R_1% (air)	R_2% (air)	Grain 2 R_1% (air)	R_2% (air)	Grain 1 R_1% (oil)	R_2% (oil)	Grain 2 R_1% (oil)	R_2% (oil)
400	23.6	24.3	22.8	23.4	10.8	11.2	9.3	9.7
420	23.6	24.3	22.9	23.4	10.7	11.1	9.2	9.6
440	23.5	24.2	22.7	23.2	10.5	10.8	8.9	9.4
460	23.3	23.8	22.3	22.9	10.3	10.6	8.6	9.0
480	22.8	23.4	22.0	22.5	9.9	10.2	8.3	8.7
500	22.4	23.0	21.6	22.1	9.5	9.8	8.0	8.4
520	21.9	22.5	21.2	21.7	9.2	9.5	7.75	8.1
540	21.5	22.1	20.9	21.4	8.8	9.1	7.5	7.9
560	21.1	21.7	20.45	21.0	8.5	8.8	7.2	7.6
580	20.7	21.3	20.2	20.6	8.2	8.5	7.0	7.3
600	20.5	21.0	19.9	20.4	8.0	8.3	6.8	7.1
620	20.2	20.7	19.6	20.1	7.8	8.0	6.65	7.0
640	19.9	20.4	19.3	19.8	7.6	7.85	6.5	6.9
660	19.7	20.1	19.1	19.6	7.45	7.7	6.4	6.7
680	19.5	19.9	18.8	19.3	7.2	7.4	6.3	6.6
700	19.4	19.7	18.6	19.0	7.1	7.25	6.3	6.4

COLOR VALUES: C ILLUMINANT

	x	y	Y%	P_e%	λ_d
Grain 1 (air)					
R_1	0.290	0.306	21.2	5.4	479
R_2	0.298	0.306	21.8	5.4	479
Grain 2 (air)					
R_1	0.299	0.307	20.6	5.0	479
R_2	0.299	0.307	21.1	5.0	479
Grain 1 (oil)					
R_1	0.288	0.295	8.61	10.6	479
R_2	0.288	0.296	8.89	10.5	479
Grain 2 (oil)					
R_1	0.289	0.296	7.31	10.1	478
R_2	0.289	0.296	7.67	10.0	478

The spectra were obtained with a Zeiss Axiotron MPM80 spectrophotometer. The objectives used were Epiplan Neofluars X50, eff.N.A. 0.30, with Zeiss oil for immersion ND = 1.515, and the reflectance standard was Zeiss SiC (no. 472). The diameter of the measuring spot was set at 8 micrometers. Grain 1: see representative compositions 1 and 5; grain 2: number 3, Table 6.

skeletal habit), an oxidizing fluid may have had access to the central part of this crystal and, thus, the grain began to oxidize, and the Pd–Pb oxide crystallized, from the center to the periphery. The oxidation was incomplete, and relics of the grains are preserved as the rim. The second interpretation is that the pre-existing crystal of zvyagintsevite was completely replaced by the Pd–Pb oxide; however, its subhedral (pseudomorphous: *cf.* Fig. 9A) outlines remained. At a later stage, the oxide reacted with a reducing fluid (*e.g.*, containing H_2 as reducing agent) and was reduced back to the zvyagintsevite.

Reflectance and infrared-absorption spectroscopy

Under reflected light in air, the Pd–Pb oxide is gray and has a low reflectance. Compared with "palladinite" from the type locality, which is distinctly bireflectant and anisotropic (J. Jedwab *et al.*, unpubl. data), the Pd–Pb oxide has a distinctly lower reflectance, and, in contrast, shows no bireflectance and anisotropy (Fig. 11). Reflectance data obtained for two grains of the Pd–Pb oxide indicate that it is isotropic or nearly so (Table 5).

The existence of a synthetic $PdO \cdot xH_2O$ phase (PDF 9–254) stimulated us to test whether or not the Pd–Pb oxide also is hydrous. Owing to the small grain-size, infrared-absorption spectroscopy studies of natural *PGE* oxides are complicated, and we are not aware of results of similar studies in the literature. The infrared spectrum of the Penikat Pd–Pb oxide was obtained using a Spectra-Tech IR-Plan infrared microscope interfaced to a Bomem Michelson MB–120 Fourier-transform infrared spectrometer, which utilizes a 0.25 mm liquid-nitrogen-cooled mercury–cadmium telluride detector. A very small amount of the pure material (from a grain ~0.2 mm in size) was dug out of polished section and mounted in a diamond-anvil microsample cell. Pressure was then applied to crush the mineral and cause it to spread as a randomly oriented powder; after crushing, the pressure was released. The diamond cell was then positioned in the microscope accessory, and the powdered sample masked, so as to isolate a circular area measuring 100 μm in diameter and between 1 and 5 μm in uniform thickness. Two hundred scans were collected and added together, at 4 cm^{-1} resolution, from 700 to 4000 cm^{-1}. The transmittance spectrum was produced by taking the ratio of the single-beam spectrum of the specimen in the diamond-anvil cell against a single-beam spectrum of the empty diamond-anvil cell collected with the same parameters. The spectrum obtained (Fig. 12) is virtually devoid of any bands; there is abso-

TABLE 6. CHEMICAL COMPOSITION OF UNNAMED Pd–Pb OXIDE FROM THE PENIKAT LAYERED COMPLEX, FINLAND

No.	1§	2§	3§	4*	5*	6*	7**
PdO wt.%	81.91	80.29	76.56	79.86	80.83	82.85	80.38
PbO	17.44	18.11	21.39	19.10	18.59	18.89	18.92
Total	99.35	98.40	97.95	98.96	99.42	101.74	99.30
Atomic proportions (O = 10)							
Pd *apfu*	8.955	8.90	8.67	8.84	8.88	8.89	8.86
Pb	1.045	1.10	1.33	1.16	1.12	1.11	1.14
Atomic proportions (O = 1)							
Pd *apfu*	0.90	0.89	0.87	0.88	0.89	0.89	0.89
Pb	0.10	0.11	0.13	0.12	0.11	0.11	0.11

§ JEOL–733 electron microprobe, an accelerating voltage of 15 kV and a probe current of 15 nA. The following lines (standards) were used: Pd*Lα*, Pt*Lα* and Pb*Lα* (pure metals and PbTe).
* Cameca Camebax electron microprobe, an accelerating voltage of 20 kV and a probe current of 23 nA. The following lines (standards) were used: Pd*Lα*, Pt*Mα* and Pb*Mα* (pure metals and PbS). Pt was sought, but not detected.
** Average result of six analyses (1 to 6).

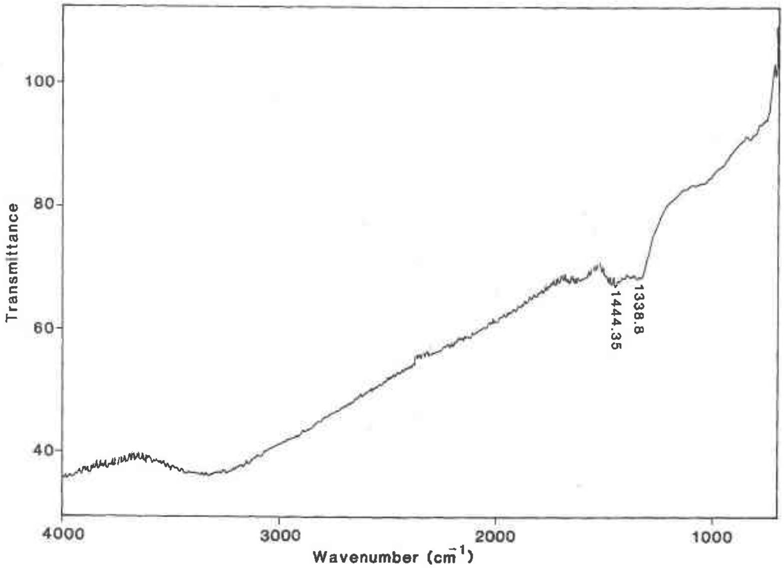

FIG. 12. Infrared-absorption spectrum of the unnamed Pd–Pb oxide from Penikat.

lutely nothing in the regions where one would expect bands ascribable to H_2O or OH groups. For this reason, we infer that the Pd–Pb oxide is anhydrous.

Composition

Relatively large grains of the Pd–Pb oxide were examined and analyzed with the SEM–EDS, and were found to contain Pd, Pb and O. A large number of quantitative EDS analyses reveal relatively narrow compositional ranges for Pd and Pb, which are rather homogeneously distributed. Results of two sets of WDS electron-microprobe analyses of the oxide (large grains), obtained using different instruments, standards and analytical conditions, are in good agreement with each other (Table 6).

In addition to the large grains, small grains of the Pd–Pb oxide (from a chain-like veinlet) and the microcrystalline aggregate (Fig. 10) were analyzed with EDS. Essential concentrations of Cu (up to 4.8 wt.% CuO), Fe (0.7–1.6 wt.% FeO) and Pt (up to 1.7 wt.% PtO_2) were recorded. The compositional variation observed $[(Pd_{7.8-8.0}Cu_{0.6-0.8}Fe_{0.1-0.3}Pt_{0.05-0.10})_{\Sigma 8.8-9.0}Pb_{0.9-1.1}O_{10}]$ suggests that elements other than Pd (Cu, Fe, and Pt) may replace ~1 Pd atoms per formula unit (*apfu*). The elevated Cu concentration cannot be ascribed to contamination by the host; the hydrous silicate is totally devoid of Cu. Zvyagintsevite crystals from this ore deposit are poor in Cu; thus, the Cu in the oxide was probably contributed from a fluid during oxidation. As a more remote possibility, it may reflect an impurity in the fine-grained material analyzed. We recall that Olivo & Gauthier (1995) reported up to 8.4 wt.% CuO (and up to 1.3 wt.% Fe_2O_3) in the "palladinite" from Brazil.

Electron-microprobe results suggest a generalized formula Pd_9PbO_{10} or (Pd,Pb)O for the Penikat oxide. The phase Pd_9PbO_{10} has apparently never been synthesized. The only Pd–Pb oxides reported are $PdPbO_2$, whose X-ray powder pattern (PDF 38–1357) is substantially different from that of the Kirakkajuppura material, and Pd_9PbO_{19} (Machida *et al.* 1984). No XRD data are available for the latter phase, which also displays the ratio Pd:Pb of 9 but is richer in O and differs in the oxidation state of Pd (*i.e.*, Pd^{4+} *versus* Pd^{2+}). A relationship between the natural $Pd^{2+}{}_9Pb^{2+}O_{10}$ and synthetic $Pd^{4+}{}_9Pb^{2+}O_{19}$ may exist.

Pd and Pb are commonly divalent, and both the formulae $(Pd_{0.9}Pb_{0.1})O$ and Pd_9PbO_{10} are thus possible in terms of charge balance. Three major arguments favor the choice of the latter formula. (1) Isomorphous relationships between Pd and Pb are highly unusual. (2) All

TABLE 7. X-RAY POWDER-DIFFRACTION DATA FOR THE UNNAMED Pd–Pb OXIDE FROM THE PENIKAT COMPLEX, FINLAND

I (est.)	*d* (Å)	I (est.)	*d* (Å)	I (est.)	*d* (Å)
10 *vb*	2.69	1	2.04	1 *b*	1.55
3	2.35	0.5	1.82	1	1.44
0.5	2.17	1 *vb*	1.68	1 *vb*	1.33

The pattern obtained using a 57.3 mm Debye–Scherrer camera, Cu radiation, Ni filter (λ Cu$K\alpha$ = 1.54178 Å), intensities estimated visually. Not corrected for shrinkage and no internal standard. *b*: broad line, *vb*: very broad line.

the Pd–Pb oxide grains analyzed so far contain about the same (high) level of Pb, *i.e.* ~1 *apfu* Pb (O=10); this characteristic implies that Pb occupies a separate site in the crystal structure. (3) None of the related natural PdO-type oxides reported to date shows as high a content of a semimetal as does this Pd–Pb oxide. Nevertheless, the formula (Pd,Pb)O is still a possibility to be tested.

X-ray study

X-ray powder data for the Pd–Pb oxide are presented in Table 7. The mineral is cryptocrystalline, as was revealed in an attempted precession single-crystal study, and produces rather broad diffuse arcs on the powder film. For this reason, we chose to measure the pattern obtained with a 57.3 mm Debye–Scherrer camera. It exhibits important differences with respect to both the tetragonal and cubic polymorphic modifications of PdO (*cf.* PDF 43–1024 and 46–1211).

DISCUSSION

The Kirakkajuppura *PGE* deposit of the Penikat layered complex is rather unique among *PGE*-mineralized occurrences in layered intrusions, even those of the low-sulfide type. The deposit shows examples of unusually *PGE*-rich mineralization, which occurs in nearly *BMS*-free rock and does not display a close relationship with accessory chromite. In many related complexes, for instance at Bushveld (Von Gruenewaldt *et al.* 1986) and Rathbun Lake (Rowell & Edgar 1986), most of the *PGM* are enclosed by hydrous silicates, although their close spatial association with *BMS* or chromitite (or both) is characteristic. Furthermore, the deposit contains exceedingly high (*e.g.*, ~0.5 kg/t total *PGE*; Table 3) maximum concentrations of the *PGE*, mainly Pd and Pt, in very S-poor (and relatively Cr-poor) samples. The maximum enrichment in *PGE* is at least one order of magnitude higher than that reported from the Merensky-type and related ores worldwide, and is quite comparable with *PGE* grades found in dunite pipes of the Bushveld complex, in which the highest concentrations of *PGE* among layered intrusions are recorded (*e.g.*, Naldrett 1981). The relative abundance of late-stage vysotskite – braggite in the form of unusually large aggregates (Fig. 5A), the general absence or scarcity of *BMS* at Kirakkajuppura, and the atomic ratio (Pd + Pt)/S close to 1 in the bulk-rock compositions indicate that nearly all S in the *PGE*-rich samples is contributed by the *PGE*-bearing sulfides. This contrasts with observations from other parts of the Sompujärvi reef, in which S-free *PGM* predominate (Alapieti & Lahtinen 1986, Halkoaho 1993).

Another distinctive feature of the Kirakkajuppura mineralization is the relative abundance of Pb-rich *PGM* (zvyagintsevite, unnamed Pd–Pb oxide, Pd-rich konderite and previously unknown $Pd_3Pb_2S_2$). The presence of Cu–Fe–*PGE* thiospinels (Barkov *et al.* 2000) also is unusual, as these are typically associated with Ural–Alaska-type complexes. In other layered intrusions, a few minor occurrences of zvyagintsevite have been reported (*e.g.*, unpubl. report of Laflamme 1976, cited in Szymański *et al.* 1997, Barkov *et al.* 1991); this *PGM* is rather characteristic of other types of *PGE* deposits, such as the Noril'sk (Genkin *et al.* 1966, Cabri & Traill 1966) and the Konder alkali-ultramafic complex, in which, in related placers, unusually large (8 mm) crystals of zvyagintsevite occur (Cabri & Laflamme 1997). The location of the Kirakkajuppura deposit relatively close to the wallrocks (Fig. 2) may imply that contamination of the magma was responsible for the relative abundance of the Pb-rich *PGM* in the deposit. A test of this possibility awaits isotopic data. The only relevant available data concern another Finnish layered intrusion, Suhanko–Konttijärvi (Portimo complex, Fig. 1); there, the Pb isotopic composition of galena from the marginal series provides evidence for contamination (Alapieti *et al.* 1989).

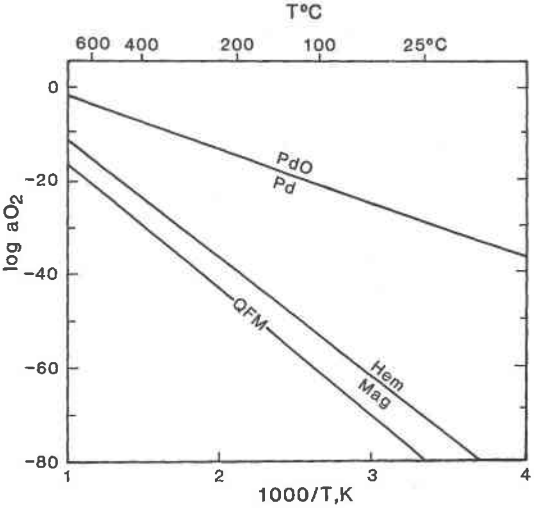

FIG. 13. Log $a(O_2)$ – T diagram showing position of the Pd–PdO buffer, compared with magnetite–hematite (Mag–Hem) and quartz – fayalite – magnetite (QFM) buffers (Olivo & Gammons 1996, and references therein).

Textural relationships (Fig. 7) suggest a low-temperature crystallization for the Kirakkajuppura zvyagintsevite, after associated Pd-rich vysotskite – braggite, which itself is of low-temperature origin. According to experimental data (Cabri *et al.* 1978), vysotskite can only crystallize at a subsolidus temperature. The last *PGM* to form in this mineral assemblage is, in general, the Pd–Pb oxide.

The Penikat *PGE* oxide contains a significant amount of an element other than Pd and O. Similarly, other natural *PGE* oxides contain a wide variety of minor elements, such as Cu, Fe, Ni, Mn and Hg (Clark *et* *al.* 1974, Jedwab *et al.* 1993, Augé & Legendre 1994, Olivo & Gauthier 1995, Garuti *et al.* 1997, Krstić & Tarkian 1997). Apart from Mn and some base metals, most of these elements in *PGE* oxides are inherited from their precursors, the primary *PGM*. The incorporation of these elements may well stabilize *PGE* oxides (*cf.* Westland 1981).

The oxidation reactions

"Palladinite", the related Pd–(Cu–Fe) oxide, formed during recent weathering *via* oxidation of palladseite ($Pd_{17}Se_{15}$) to metallic Pd and subsequent oxidation of the Pd to PdO (Olivo & Gammons 1996). Although the Pd–PdO reaction requires a very high fugacity of oxygen, a lower $f(O_2)$ would be needed to form PdO at lower temperatures (Fig. 13). In New Caledonia, the complex *PGE* oxides formed in lateritic conditions (Augé & Legendre 1994). However, the Penikat Pd–Pb oxide may have had a different origin. It appears to have formed during a very late-stage event of deuteric hydrothermal alteration, as a result of oxidation of zvyagintsevite by strongly oxygenated fluids at low temperatures. A change in volume during the conversion of the zvyagintsevite may have resulted in the strongly fractured appearance of the Pd–Pb oxide (Fig. 9A).

Various reactions to produce the Pd–Pb oxide may be proposed. It may have been formed in two stages. The first stage would have resulted in the formation of pure Pd, which, owing to further oxidation by the fluids (second stage), would have then been converted to the Pd–Pb oxide. Two possible mechanisms of oxidation exist, with H_2O or without H_2O, respectively:

$$6Pd_3Pb + 2O_2 + 2H_2O = 18Pd + 6PbO + 2H_2$$

The release of hydrogen would lead to locally reducing micro-environment.

$$18Pd + 9O_2 + 2PbO = 2Pd_9PbO_{10}.$$

The availability of H_2O is consistent with the intimate association of the ore minerals with hydrous silicates. The rest of the PbO (*i.e.*, 4PbO) may have been incorporated in the associated Pb–V oxide, according to the simple reaction $4PbO + V_2O_5$ (fluid) $= Pb_4V_2O_9$, which took place during a late-stage oxidizing event when a fluid infiltrated the cleavage in the amphibole (Fig. 8).

The second possible mechanism of conversion may be represented as:

$$6Pd_3Pb + 3O_2 = 18Pd + 6PbO$$

and

$$18Pd + 9O_2 + 2PbO = 2Pd_9PbO_{10}.$$

No remnants of the pure Pd were observed, however, and the zvyagintsevite might thus be directly converted to the Pd–Pb oxide, according to a hypothetical reaction:

$$3Pd_3Pb + 6O_2 = Pd_9PbO_{10} + 2PbO.$$

Petrogenetic aspects

A strong partitioning of *PGE* into a segregating sulfide liquid is believed to have played an important role in the formation of stratiform *PGE* deposits in layered intrusions (*e.g.*, Campbell *et al.* 1983, Naldrett *et al.* 1990). The partition coefficients of the *PGE* in favor of sulfide liquid over basaltic liquid are high; *e.g.*, 17 (± 7) $\times 10^3$ and 10 (± 4) $\times 10^3$ for Pd and Pt, respectively (Fleet *et al.* 1996), and, in the case of a high Ni content in sulfide fraction, 28 (± 12.5) $\times 10^3$ and 16.5 (± 6.3) $\times 10^3$ (Crocket *et al.* 1997), respectively. In spite of these values, the extremely *PGE*-rich and S-poor mineralization at Kirakkajuppura could not have formed as a consequence of the collection of *PGE* by a magmatic sulfide liquid *in situ*. Textural relationships (*e.g.*, Figs. 5, 7) strongly suggest the hydrothermal deposition of the *PGE* minerals from a volatile-rich phase which, at least locally, may have been mobile. The veinlet-(chain)-like aggregates of *PGM* that we described likely precipitated directly from the fluid phase, in sites controlled by systems of micro fractures in the rock and by the cleavage of the hydrous silicates. The strongly heterogeneous distribution of the *PGM* in the ore deposit and the abundance of pegmatitic rocks in the area (Figs. 3, 4) also support this suggestion.

Theoretical considerations suggest that Pd and Pt may be mobile in the form of bisulfide complexes in H_2S-rich aqueous solutions under reducing conditions and at various temperatures (*e.g.*, Gammons & Bloom 1993, Pan & Wood 1994, Wood *et al.* 1994), and that the relevant Pd–Pt sulfides are relatively soluble as bisulfide complexes even at temperatures as low as 25°C (Wood *et al.* 1989). Recently, Pd and Pt sulfides have been synthesized at temperatures below 100°C under reducing conditions (Tarkian *et al.* 1996). Chloride complexing of *PGE* also may be of importance in transporting them under hydrothermal conditions; however, this would require a relatively hot, saline, and acidic fluid and a strongly oxidized environment (*e.g.*, Gammons *et al.* 1992). Chlorine is interpreted to have been a likely agent for transport and deposition of *PGE* in some ore deposits (*e.g.*, Boudreau & McCallum 1992, Li & Naldrett 1993, Olivo & Gammons 1996). No evidence for a Cl-rich environment at Kirakkajuppura has been found, however. Three subhedral crystals of apatite (up to 20 μm), found in the section containing the largest aggregates of *PGM* (Fig. 5), are very poor in Cl ($\leq$0.2 wt.% Cl). The amphibole associated with the *PGM* is nearly Cl-free (<0.05 wt.% Cl), but its composition (poor in Fe, K and Al) indicates that this feature may well be due to crystallochemical constraints (*cf.* Oberti *et al.* 1993), rather than to a Cl-depleted environment.

The efficient preferential incorporation of Pd, relative to Pt and to other *PGE*, into hydrothermal fluids is implied by the Pd-rich character of the Kirakkajuppura mineralization and by the high-Pd compositions of the late-stage *PGM* (vysotskite – braggite series, zvyagintsevite and keithconnite). The predominance of the S-rich *PGM* and their intimate association with the hydrous silicates are consistent with the theoretical predictions that Pd and Pt may be mainly transported as bisulfide complexes and deposited from H_2S-rich, weakly oxidized or reduced aqueous fluids at relatively low temperatures. Most of the late-stage *PGE* sulfides in the ore deposit could be formed under such conditions, during an early stage of hydrothermal activity. The Pd-rich composition of the late-stage vysotskite – braggite is in good agreement with the experimental data (Cabri *et al.* 1978), which indicate a higher-temperature character of Pt-rich members of the series relative to vysotskite (Pd-rich). In general, the local hydrothermal system at Kirakkajuppura may have evolved toward a S-poor and more oxidized environment. We contend that at a later stage of crystallization, zvyagintsevite and related phases partly replaced the vysotskite – braggite, the zvyagintsevite chains were formed, and the submicrometric zvyagintsevite precipitated as subparallel grains from fluids that percolated along the cleavage in the hydrous silicates (Fig. 7). At the final stage of hydrothermal alteration, the Pd–Pb oxide appeared as a result of the interaction of the zvyagintsevite with the latest, more strongly oxygenated fluids.

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