A POTENTIALLY NEW KONDERITE–LIKE SULFIDE OF Fe, Pb, Cu, Rh, Pd, AND Ir FROM THE PENIKAT LAYERED COMPLEX, FINLAND

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Abstract

A potentially new konderite-like sulfide of Fe, Pb, Cu, Rh, Pd, and Ir [hereafter: "Pb–(Fe)+Pd Kdr"] occurs in an intimate association with platinum-group element (PGE) thiospinel (*i.e.*, cuprorhodsite – ferrorhodsite – cuproiridsite: Cpr) in the S-poor Kirakkajuppura PGE deposit hosted by the Penikat layered complex, Finland. The "Pb–(Fe)+Pd Kdr" (a large grain, LG: 0.15 mm in size and a rim-like grain, RG) displays thiospinel-type proportions (Cu + Fe + Pb + Ni) : (Rh + Ir + Pd + Pt + Co) : S of 1 : 2 : 4, but differs from the associated Cpr in its appearance, texture and optical properties, and also in the presence of Pb (up to 9.7 wt.%) and Pd (up to 6.4 wt.%), which are positively correlated. A relationship between the "Pb–(Fe)+Pd Kdr" and konderite from the Kondyor Uralian–Alaskan–type complex [*i.e.*, $(Cu,Ni,Fe)_3Pb(Rh,Pt,Ir)_8S_{16}$: hexagonal and thiospinel-derivative) likely exists. Results of multiple electron-microprobe analyses of the "Pb–(Fe)+Pd Kdr" point to coupled Pb-for-Fe and Pd-for-Rh atomic substitution mechanisms; the Fe-rich compositions of this sulfide imply the existence of an (unnamed) Fe-dominant analogue of konderite. The approximate scheme of substitution operating in the LG appears to be $[Cu^+ + 2 (Pb + Ni)^{2+}] + 2 Pd^{2+} = 2 Fe^{3+} + Rh^{3+}]$. Also, variations in S could be essential in maintaining charge balance. In contrast, Cu is unlikely to be involved in the charge-balance substitution in the RG; in fact, Ni is more important than Cu in the RG. The LG and Cpr observed in a mutual intergrowth contain equal amounts of Ir, and, thus may have reached equilibrium in the distribution of Ir, whereas all Pb was selectively partitioned into the "Pb–(Fe)+Pd Kdr". The appearance of these thiospinel- and konderite-type chalcogenides, which are uncharacteristic of layered intrusions, is related to the anomalously S-poor character of the Kirakkajuppura PGE deposit, which is similar in this respect to the Uralian–Alaskan–type complexes.

Keywords: platinum-group elements, platinum-group minerals, chalcogenides, sulfides, thiospinels, konderite, unnamed mineral, mechanisms of substitution, mineralization, Kirakkajuppura deposit, Penikat layered complex, Finland.

Sommaire

Nous décrivons un sulfure méconnu de Fe, Pb, Cu, Rh, Pd, et Ir [ci-après: "Pb–(Fe)+Pd Kdr"], potentiellement une nouvelle espèce affiliée à la konderite trouvée en association étroite avec un thiospinelle enrichi en éléments du groupe du platine (EGP), de la série cuprorhodsite – ferrorhodsite – cuproiridsite (Cpr) dans le gisement à EGP à faible teneur en soufre de Kirakkajuppura, que renferme le complexe stratiforme de Penikat, en Finlande. Cette phase, présente surtout en deux grains, un plus gros (0.15 mm) et l'autre en bordure d'un grain de Cpr, fait preuve de proportions de cations rappelant un thiospinelle: (Cu + Fe + Pb + Ni):(Rh + Ir + Pd + Pt + Co):S égal à 1:2:4, mais s'en distingue par son apparence, sa texture rubannée et ses propriétés optiques, et aussi par la présence de Pb (jusqu'à 9.7%, poids) et Pd (jusqu'à 6.4%), dont la corrélation entre teneurs est positive. Une relation entre la phase "Pb–(Fe)+Pd Kdr" et la konderite découverte dans le complexe de Kondyor, de type Ourale–Alaska [dont la composition est $(Cu,Ni,Fe)_3Pb(Rh,Pt,Ir)_8S_{16}$: phase hexagonale et dérivée du thiospinelle] paraît vraisemblable. Les résultats d'analyses effectuées à la microsonde électronique semblent indiquer des substitutions couplées de Fe-par-Pb et Rh-par-Pd; les compositions riches en fer de ce sulfure laissent prévoir l'existence d'un analogue de la konderite à dominance de Fe. Le schéma de substitution dans le plus gros des grains peut se résumer ainsi: $[Cu^+ + 2 (Pb + Ni)^{2+}] + 2 Pd^{2+} = 2 Fe^{3+} + Rh^{3+}]$. De plus, des variations en S pourraient s'avérer essentielles pour maintenir l'électroneutralité. En revanche, le Cu ne semble pas impliqué dans la substitution dans le moins gros des grains. En fait, le Ni serait plus important que le Cu dans ce cas. Le plus gros des grains et

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le thiospinelle (Cpr), observés en intercroissance, contiennent des quantités équivalentes d'iridium, et seraient donc équilibrés, mais tout le Pb est réparti sélectivement dans le "Pb–(Fe)+Pd Kdr". La présence ici de ces chalcogénures de type thiospinelle et konderite, qui ne sont pas caractéristiques de massifs stratiformes, traduit la pauvreté en soufre des roches du gisement de Kirakkajuppura, qui ressemble de ce point de vue les complexes de type Ourale–Alaska.

(Traduit par la Rédaction)

Mots-clés: éléments du groupe du platine, minéraux du groupe du platine, chalcogénures, sulfures, thiospinelles, konderite, minéral sans nom, mécanismes de substitution, minéralisation, gisement de Kirakkajuppura, complexe stratiforme de Penikat, Finlande.

Introduction

The present study is part of a research project on various platinum-group minerals (PGM) and their associations in the Kirakkajuppura platinum-group element (PGE) deposit, hosted by the Penikat complex, Finland. This mafic–ultramafic complex of an Early Proterozoic age is a typical layered intrusion (Alapieti & Lahtinen 1986, Halkoaho *et al.* 1990, Alapieti & Halkoaho 1995). The Kirakkajuppura deposit, on the other hand, is extraordinary in the presence of exceptionally high concentrations of the PGE in altered S-poor mafic–ultramafic rocks, resulting in numerous unusual species of PGM. No analogue of this deposit is known in other layered intrusions. This paper is a contribution to the platinum-group mineralogy of the Kirakkajuppura deposit.

In this paper, we report on the occurrence and characteristics of a potentially new sulfide of Fe, Pb, Cu, Rh, Pd and Ir. This sulfide mineral is similar to PGE-rich thiospinels in composition and displays the atomic proportions (Cu + Fe + Pb + Ni) : (Rh + Ir + Pd + Pt + Co) : S of 1 : 2 : 4, in common with the PGE thiospinels. On the other hand, it is distinct from the associated thiospinels in its characteristic appearance, texture and optical properties, and also in the presence of significant concentrations of Pb (up to 9.7 wt.%) and Pd (up to 6.4 wt.%). These elements are involved in a coupled substitution, as also is reported in this paper. We are not aware of any thiospinels or compounds related to thiospinels that exhibit covariance between Pb and Pd. This sulfide of Fe, Pb, Cu, Rh, Pd, and Ir seems related to konderite, hexagonal $(Cu,Ni,Fe)_3Pb(Rh,Pt,Ir)_8S_{16}$ with a thiospinel-derivative structure, reported only from the Kondyor (Konder) Uralian–Alaskan-type complex, Aldan Shield, northeastern Russia (Rudashevskii *et al.* 1984b). In contrast to konderite, which has a uniform composition, the konderite-like sulfide from Kirakkajuppura [hereafter: "Pb–(Fe)+Pd Kdr"] displays considerable Fe $\leftrightarrow$ Pb and Rh $\leftrightarrow$ Pd substitution, the Fe-rich portions apparently corresponding to a potential Fe-dominant analogue of konderite [$(Cu,Ni,Fe)_{3+x}$ $(Fe,Pb)(Rh,Ir,Pd)_{8-x}S_{16}$, where $x < 0.5$]. The present study thus extends our knowledge of the crystal chemistry of the extensive family of thiospinels and thiospinel-derivative compounds.

Occurrence and Associated Minerals

Mineralization at Kirakkajuppura is associated with the Sompujärvi PGE reef, occurring in a completely altered pyroxenite and the adjacent gabbroic and peridotitic rocks, at the northern end of the Penikat complex, at the contact between peridotitic–pyroxenitic and gabbroic cumulates (Alapieti & Lahtinen 1986, Halkoaho *et al.* 1990, Alapieti & Halkoaho 1995). The grain size of the PGM in this unique deposit varies from submicrometric to ~1 cm mega-aggregates, which are veinlet-shaped and erratically distributed among hydrous silicates, including actinolite ($\geq$70 vol.%), subordinate clinochlore, and minor zoisite or clinozoisite (Barkov *et al.* 1999). Disseminated chromite ($\leq$10%) is distributed heterogeneously in the PGE-rich mineralized rock, which can be virtually devoid of base-metal sulfides (BMS). Grains of chalcopyrite, bornite, millerite, and secondary chalcocite (grains $\leq$0.3 mm) are occasionally observed. The other accessories are titanite, apatite (Cl-poor) and an unnamed Pb–V oxide [Pb_4O $(VO_4)_2$: Barkov *et al.* (1999), Krivovichev & Burns (2003)]. Previous publications dealt with an unnamed Pd–Pb oxide ($Pd^{2+}_9Pb^{2+}O_{10}$ or $Pd^{2+}_7Pb^{2+}O_8$) formed at the expense of zvyagintsevite (Pd_3Pb) (Barkov *et al.* 1999), various PGE-rich thiospinels, members of the cuprorhodsite [$CuRh_2S_4$] – ferrorhodsite [$(Fe,Cu)(Rh,$ $Pt,Ir)_2S_4$] – cuproiridsite and cuprorhodsite – ferrorhodsite – malanite [$Cu(Pt,Ir,Rh)_2S_4$] series (Barkov *et al.* 2000), laflammeite, a new species ($Pd_3Pb_2S_2$: Barkov *et al.* 2002), and variously zoned PGE sulfides and sulfarsenides of the laurite (RuS_2) – erlichmanite (OsS_2), vysotskite (PdS) – braggite (Pt,Pd)S, and irarsite (IrAsS) – hollingworthite (RhAsS) series (Barkov *et al.* 2004). The Pd–Pt sulfides (vysotskite–braggite series) strongly predominate over the other PGM, and, typically, most of the S in the PGE-rich (BMS-poor) samples is contained in the PGE sulfides (Barkov *et al.* 1999). Also present are keithconnite ($Pd_{20}Te_7$), a Pb-rich variant of keithconnite(?) [$Pd_{20}(Te_6Pb)$], unnamed Rh(Ni,Fe, $Cu)_2S_3$, the Pd-dominant analogue of hongshiite (?) [(Pd,Pt)Cu], and Pd-rich gold (up to 9 wt.% Pd).

OBSERVATIONS AND TEXTURES

The "Pb–(Fe)+Pd Kdr" is intimately associated with PGE thiospinels of the cuprorhodsite – ferrorhodsite – cuproiridsite series (Cpr). This sulfide occurs (1) in a large grain in which it is intergrown with Cpr (Fig. 1A), (2) fine lamellae (apparently crystallographically ori-

ented) in the Cpr (Fig. 1A), (3) as a rim-like grain located at the periphery of a composite grain of various PGM (Fig. 1B), and (4) as small inclusions within (or at the border of) a PGE thiospinel grain (Cpr: Fig. 1C). A minute inclusion of a Pd-rich telluride a few μm in size, with a Pd:Te ratio of approximately 3:1, based on quantitative energy-dispersion (EDS) data, and thus possi-
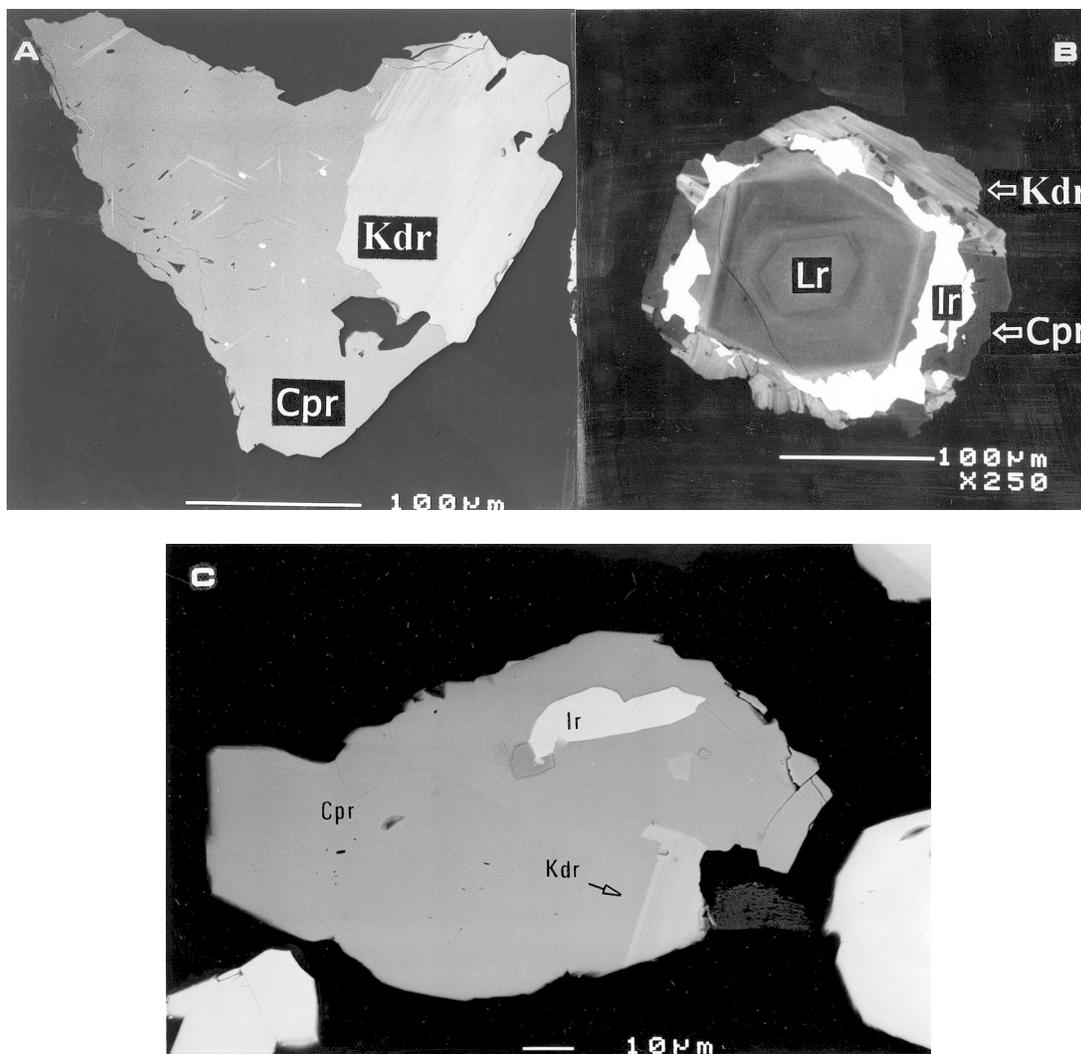

FIG. 1. A. An intergrowth of the konderite-like sulfide of Fe, Pb, Cu, Rh, Pd and Ir (Kdr) with a PGE-rich thiospinel of the cuprorhodsite – ferrorhodsite – cuproiridsite series [(Cu,Fe)(Rh,Ir)$_2$S$_4$] (Cpr). Note the presence of fine exsolution-induced lamellae of the konderite-like sulfide in the grain of cuprorhodsite – ferrorhodsite – cuproiridsite. B. A complexly zoned grain of various PGM, consisting of zoned laurite–erlichmanite in the center (Lr), mantled by cryptically zoned irarsite–hollingworthite (Ir), cuprorhodsite – ferrorhodsite – cuproiridsite (Cpr), and the konderite-like sulfide of Fe, Pb, Cu, Rh, Pd, and Ir (Kdr). C. The textural relationship between cuprorhodsite – ferrorhodsite – cuproiridsite (Cpr) and the konderite-like sulfide of Fe, Pb, Cu, Rh, Pd, and Ir (Kdr). Irarsite–hollingworthite (Ir: white) occurs intergrown with a minute grain of laurite(?) (gray). Back-scattered electron images. The samples are from the Kirakkajuppura PGE deposit, Penikat complex. The surrounding material is epoxy.

bly keithconnite, was observed in the "Pb–(Fe)+Pd Kdr".

In reflected light, in an intergrowth with the PGE thiospinel (Fig. 1A), the "Pb–(Fe)+Pd Kdr" is cream-colored, with a higher reflectance than the associated thiospinel, which appears gray with a slight bluish tint. The "Pb–(Fe)+Pd Kdr" seems to display a very weak optical anisotropy. Its grain boundaries with the Cpr are characteristically sharp. Compositional zoning is not apparent. It invariably displays a "finely layered" texture, however, the individual "layers" being a few μm thick and having diffuse boundaries. This feature is well displayed in back-scattered electron images, and possibly reflects variations in Pb and Fe (Figs. 1A, C). The "Pb–(Fe)+Pd Kdr" thus may have a layered microstructure; in addition, some grains seem to display fine twinning. Alternatively, and more likely, this texture probably implies the presence of oscillatory zoning, which is relatively common in various minerals, including some sulfides (*e.g.*, Shore & Fowler 1996, Halden 1996, and references therein).

The large grain of the "Pb–(Fe)+Pd Kdr" shown in Figure 1A was carefully re-polished (courtesy of the late Dr. A.J. Criddle). This step removed a layer at least 20 μm thick. Although the outline of the grain in the polished mount changed somewhat, its textural features and observed zoning remained essentially unchanged.

ELECTRON-MICROPROBE ANALYSES

The konderite-like sulfide and associated Cpr were analyzed with wavelength-dispersion spectrometry (WDS) using a JEOL JXA–8900 electron microprobe operated at 20 kV and 30 nA, with a finely focused beam (<2 μm). Most of the compositional data were obtained along detailed electron-microprobe profiles, with a step interval of 1 to 5 μm. The following X-ray lines and the set of standards were used: Rh$L\alpha$, Pd$L\beta$, Ir$L\alpha$, Pt$L\alpha$ (pure metals), Pb$M\alpha$ (PbS), Co$K\beta$ [(Co,Ni)As], Cu$K\beta$, Fe$K\beta$, S$K\alpha$ (CuFeS$_2$), and Ni$K\alpha$ [(Fe,Ni,Co)$_9$S$_8$: 1.5 wt.% Co]. The Pd$L\beta$ line was used instead of the Pd$L\alpha$ in order to eliminate overlap between the emission lines of Rh and Pd. The initial results were processed by a ZAF (JEOL) on-line program. Metallic Rh and Pd standards were analyzed using the same procedure, and results of this test have confirmed that the analytical data in the present study have been not influenced by the Rh–Pd overlap. The minimum detection-limits for Pt and Co, and for Ni were ≤0.1 and ≤0.05 wt.%, respectively.

RESULTS AND DISCUSSION

Compositional variations of the "Pb–(Fe)+Pd Kdr"

Results of multiple WDS analyses of the "Pb–(Fe)+Pd Kdr" indicate a proportion (Cu + Fe + Pb + Ni) : (Rh + Ir + Pd + Pt + Co) : S of 1 : 2 : 4, suggestive of a general similarity in composition with PGE thiospinels

and konderite (Figs. 2A–C). Selected results of these analyses are listed in Tables 1 and 3, with the atomic proportions (Tables 2, 4) calculated on the basis of a total of 7 atoms (*i.e.*, thiospinel basis) and 28 atoms (*i.e.*, konderite basis) per formula unit (*apfu*). Compositional variations and element correlations observed in the large (Fig. 1A) and rim-like (Fig. 1B) grains of the "Pb–(Fe)+Pd Kdr" are shown in covariance diagrams (Figs. 3A to 5D). Representative compositions of the intergrown Cpr are given in Tables 5 and 6.

The "Pb–(Fe)+Pd Kdr" is zoned with respect to Pb, Fe, Rh and Pd, as revealed in back-scattered electron images and in results of electron-microprobe analyses (Tables 1, 3). Interference from the associated Cpr is considered unlikely because of the relatively large grain-size of the "Pb–(Fe)+Pd Kdr" (Fig. 1A). Also, the compositional trends observed for the two grains of the "Pb–(Fe)+Pd Kdr" (Figs. 3A to 5D) are consistently parallel or subparallel.

Ruthenium, Os, Zn, and Cr were not detected in the "Pb–(Fe)+Pd Kdr" and associated PGE thiospinel. Zinc was sought because this element is present in various thiospinels, such as kalininite [ZnCr$_2$S$_4$] (Reznitskii *et al.* 1985), and synthetic [Cu$_{1-x}$Zn$_x$Ir$_2$S$_4$] (Suzuki *et al.* 1999), and could possibly replace some Pb in the "Pb–(Fe)+Pd Kdr". Chromium occupies octahedral sites in a wide variety of synthetic thiospinels, but its incorporation in a natural thiospinel would require a fairly reducing environment.

Average compositions of the "Pb–(Fe)+Pd Kdr"

A total of 365 WDS analyses, made in various areas of the large grain shown in Figure 1A, gave the following average (in wt.%): Cu 9.35, Fe 2.67, Pb 7.88, Ni

TABLE 1. SELECTED RESULTS OF ELECTRON-MICROPROBE ANALYSES OF THE KONDERITE-LIKE SULFIDE FROM THE PENIKAT COMPLEX

	Cu	Fe	Pb	Ni	Rh	Pd	Ir	Co	Pt	S	Total
1	9.66	2.17	9.72	0.36	32.38	6.26	10.58	0.46	0.39	27.95	99.93
2	9.60	2.19	9.64	0.34	32.69	6.09	10.69	0.30	0.33	27.91	99.78
3	9.24	2.34	9.24	0.32	32.87	6.01	10.82	0.31	0.31	27.83	99.29
4	9.18	2.47	8.82	0.30	33.22	5.56	11.08	0.33	0.38	27.95	99.29
5	9.40	2.58	8.54	0.32	33.56	5.60	10.83	0.21	0.27	28.30	99.61
6	9.24	2.76	8.02	0.29	33.97	5.22	10.95	0.39	0.11	28.58	99.53
7	9.27	2.81	7.58	0.26	33.85	4.81	11.42	0.43	0.17	28.47	99.07
8	9.35	2.96	7.17	0.33	34.36	4.85	11.21	0.38	n.d.	29.36	99.97
9	9.25	3.08	6.82	0.33	34.70	4.91	10.56	0.51	0.27	29.53	99.96
10	9.53	3.33	6.20	0.23	35.00	4.46	11.29	0.28	0.10	29.44	99.86
11	9.33	3.48	5.93	0.27	35.80	4.20	10.28	0.39	0.21	30.02	99.91
12	9.31	3.48	5.63	0.21	35.89	4.15	10.67	0.46	0.24	29.89	99.93
13	9.19	3.56	5.21	0.24	35.57	3.85	11.38	0.45	0.19	29.79	99.43
14	9.29	3.67	4.92	0.21	36.20	3.70	10.56	0.32	0.09	30.23	99.19
15	9.32	3.99	4.46	0.20	36.72	3.42	11.25	0.45	0.13	30.31	100.25

The analytical results (in wt.%) are listed in order of decreasing content of Pb and refer to the large grain (labeled Kdr) shown in Figure 1A. See the text for analytical conditions. n.d.: not detected.

0.31, Rh 33.90, Pd 5.26, Ir 10.88, Co 0.36, Pt 0.20, S 28.73, and total 99.54. This composition corresponds to the following formulae: (1) $[(Cu_{0.65}Fe_{0.21}Pb_{0.17}Ni_{0.02})_{\Sigma 1.05}$ $(Rh_{1.46}Ir_{0.25}Pd_{0.22}Co_{0.03})_{\Sigma 1.96}$ $S_{3.98}$ $(\Sigma atoms = 7:$ thiospinel basis)] or (2) $[(Cu_{2.61}Fe_{0.30}Ni_{0.09})_{\Sigma 3.00}$ $(Pb_{0.68}Fe_{0.55})_{\Sigma 1.23}$ $(Rh_{5.85}Ir_{1.01}Pd_{0.88}Co_{0.11}Pt_{0.02})_{\Sigma 7.87}$ $S_{15.91}$ (Σatoms = 28: konderite basis)]. With formula (2), we assume that (Cu + Ni + Fe) is equal to 3 *apfu*, and that Fe enters both the Pb and Cu sites.

Twenty WDS analyses of the rim-like grain of the "Pb–(Fe)+Pd Kdr" (area shown by the white arrow in Fig. 1B) gave the following average composition (in wt.%): Cu 9.93, Fe 2.76, Pb 6.02, Ni 0.63, Rh 31.09, Pd 3.59, Ir 14.76, Co 0.44, Pt 0.65, S 29.11, and total 98.98. The formulae are (1) $[(Cu_{0.69}Fe_{0.22}Pb_{0.13}Ni_{0.05})_{\Sigma 1.09}$ $(Rh_{1.34}Ir_{0.34}Pd_{0.15}Co_{0.03}Pt_{0.015})_{\Sigma 1.88}$ $S_{4.03}]$ or (2) $[(Cu_{2.77}$ $Fe_{0.04}Ni_{0.19})_{\Sigma 3.00}$ $(Fe_{0.84}Pb_{0.52})_{\Sigma 1.36}$ $(Rh_{5.36}Ir_{1.36}Pd_{0.60}$ $Co_{0.13}Pt_{0.06})_{\Sigma 7.51}$ $S_{16.12}]$. Thus, the rim-like grain is richer in Ir (Fig. 2B), Ni, and Pt, and poorer in Rh, than the large grain. Also, the rim-like grain displays a uniform content of Cu, whereas the Cu content of the large grain

is variable, with Cu exhibiting a positive covariance with Pb (Fig. 3C). Nevertheless, both grains have parallel or subparallel compositional trends and comparable values of the correlation coefficient *R* (Figs. 3A–5D). Also, both of them seem to display a minor deficit at the

TABLE 2. ATOMIC PROPORTIONS OF THE KONDERITE-LIKE SULFIDE FROM THE PENIKAT COMPLEX

	Cu	Fe	Pb	Ni	Σ	Rh	Pd	Ir	Co	Pt	Σ	S
						7 *apfu*						
1	0.68	0.18	0.21	0.03	1.10	1.42	0.26	0.25	0.03	0.01	1.97	3.93
2	0.68	0.18	0.21	0.03	1.10	1.43	0.26	0.25	0.02	<0.01	1.97	3.93
3	0.66	0.19	0.20	0.02	1.07	1.45	0.26	0.26	0.02	<0.01	2.00	3.93
4	0.65	0.20	0.19	0.02	1.06	1.46	0.24	0.26	0.03	<0.01	2.00	3.94
5	0.66	0.21	0.18	0.02	1.07	1.46	0.24	0.25	0.02	<0.01	1.98	3.95
6	0.65	0.22	0.17	0.02	1.06	1.47	0.22	0.25	0.03	<0.01	1.97	3.97
7	0.65	0.22	0.16	0.02	1.05	1.47	0.20	0.27	0.03	<0.01	1.97	3.97
8	0.64	0.23	0.15	0.02	1.04	1.46	0.20	0.26	0.03	<0.01	1.95	4.00
9	0.63	0.24	0.14	0.02	1.03	1.47	0.20	0.24	0.04	<0.01	1.96	4.01
10	0.65	0.26	0.13	0.02	1.06	1.48	0.18	0.26	0.02	<0.01	1.94	4.00
11	0.63	0.27	0.12	0.02	1.04	1.50	0.17	0.23	0.03	<0.01	1.93	4.03
12	0.63	0.27	0.12	0.02	1.04	1.50	0.17	0.24	0.03	<0.01	1.95	4.02
13	0.63	0.28	0.11	0.02	1.04	1.50	0.16	0.26	0.03	<0.01	1.95	4.02
14	0.63	0.28	0.10	0.02	1.03	1.51	0.15	0.24	0.02	<0.01	1.92	4.05
15	0.62	0.30	0.09	0.01	1.02	1.52	0.14	0.25	0.03	<0.01	1.94	4.02
						28 *apfu*						
1	2.74	0.70	0.85	0.11	4.40	5.67	1.06	0.99	0.14	0.04	7.90	15.71
2	2.73	0.71	0.84	0.10	4.38	5.74	1.03	1.00	0.09	0.03	7.90	15.72
3	2.64	0.76	0.81	0.10	4.30	5.79	1.02	1.02	0.09	0.03	7.96	15.74
4	2.61	0.80	0.77	0.09	4.28	5.84	0.94	1.04	0.10	0.04	7.96	15.76
5	2.65	0.83	0.74	0.10	4.31	5.84	0.94	1.01	0.06	0.02	7.88	15.81
6	2.59	0.88	0.69	0.09	4.24	5.88	0.87	1.01	0.12	0.01	7.89	15.87
7	2.61	0.90	0.65	0.08	4.24	5.88	0.81	1.06	0.13	0.02	7.89	15.87
8	2.57	0.93	0.61	0.10	4.20	5.84	0.80	1.02	0.11	0.01	7.78	16.02
9	2.53	0.96	0.57	0.10	4.16	5.87	0.80	0.96	0.15	0.02	7.80	16.03
10	2.61	1.04	0.52	0.07	4.24	5.92	0.73	1.02	0.08	0.01	7.77	15.99
11	2.53	1.07	0.49	0.08	4.17	5.99	0.68	0.92	0.11	0.02	7.72	16.11
12	2.53	1.07	0.47	0.06	4.13	6.01	0.67	0.96	0.13	0.02	7.80	16.07
13	2.51	1.11	0.44	0.07	4.12	5.99	0.63	1.03	0.13	0.02	7.79	16.09
14	2.51	1.13	0.41	0.06	4.11	6.04	0.60	0.94	0.09	<0.01	7.69	16.20
15	2.50	1.22	0.37	0.06	4.14	6.08	0.55	1.00	0.13	0.01	7.76	16.10

These values of atomic proportions are calculated on the basis of a total of 7 atoms per formula unit (*apfu*) and 28 *apfu* (*i.e.*, the thiospinel-type and konderite-type formula, respectively) and pertain to the large grain (labeled Kdr) shown in Figure 1A. See Table 1 for the analytical results (in wt.%).
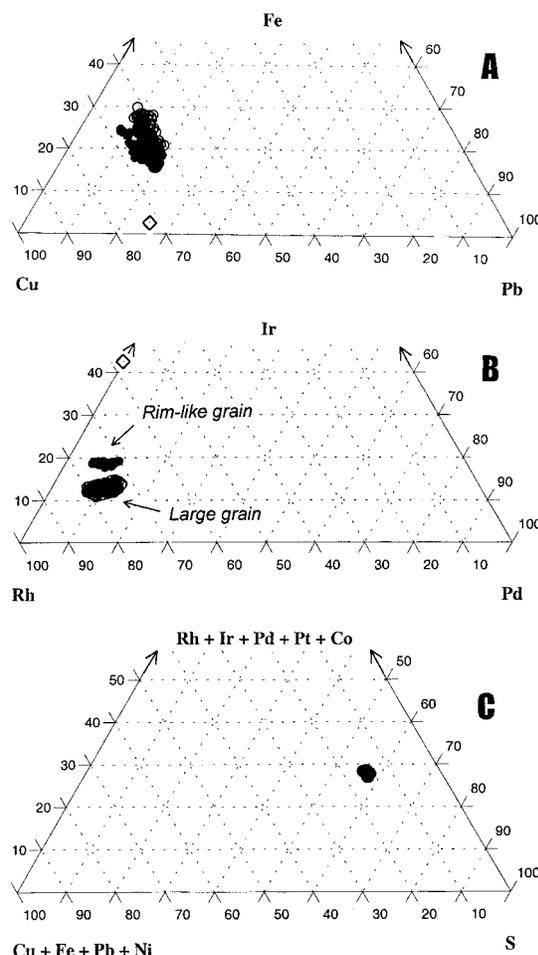
FIG. 2. Atom proportions in the konderite-like sulfide of Fe, Pb, Cu, Rh, Pd, and Ir from the Penikat complex: results of the WDS electron-microprobe analyses (in atoms per formula unit, *apfu*) projected onto the Cu – Fe – Pb (A), Rh – Ir – Pd (B) and (Cu + Fe + Pb + Ni) – (Rh + Ir + Pd + Pt + Co) – S (C) diagrams. A total of 365 analyses were made of the large grain (LG, Kdr in Fig. 1A), and 20 analyses were made of the rim-like grain (RG, Kdr in Fig. 1B). Also, the average composition of konderite from the type occurrence [*i.e.*, $Pb_{1.00}$ $(Cu_{2.81}Ni_{0.14}Fe_{0.11})_{\Sigma 3.06}$ $(Rh_{2.99}Pt_{2.80}Ir_{2.16})_{\Sigma 7.95}$ $S_{16.00}$: Rudashevskii *et al.* 1984b] is plotted for comparison (open diamond). Note that in Figure 2C, the compositions of the konderite-like sulfide from the Penikat complex (LG and RG) coincide with each other and also with the average composition of type-locality konderite.

Rh site and a relative excess at the Cu site or the Fe–Pb site.

Composition of the coexisting PGE thiospinel

It is known that cations of Cu and Fe occupy the tetrahedral (A) sites, and the PGE occupy the octahedral (B) sites in the spinel-type structure ($Fd3m$) of various thiospinels, which have the ideal formula of AB_2X_4. Results of thirty-nine analyses of the PGE thiospinel

(*i.e.*, Cpr, cuprorhodsite – ferrorhodsite – cuproiridsite: Fig. 1A) intergrown with the "Pb–(Fe)+Pd Kdr" gave the following average contents (in wt.%): Cu 9.21, Fe 5.48, Ni 0.05, Rh 40.91, Ir 11.60, Co 0.75, Pt 0.15, S 31.43, total 99.58, corresponding to the formula $[(Cu_{0.60}Fe_{0.41})_{\Sigma 1.01} (Rh_{1.64}Ir_{0.25}Co_{0.05})_{\Sigma 1.94} S_{4.05}$ (Σatoms = 7)]. The average composition of another grain of the PGE thiospinel (n = 31; Cpr in Fig. 1C), containing inclusions of the "Pb–(Fe)+Pd Kdr", is (in wt.%): Cu 9.40, Fe 5.41, Ni 0.05, Rh 41.32, Ir 11.43, Co 0.61, Pt 0.12, S 31.64, total 99.98. The corresponding formula ($Cu_{0.61}$

TABLE 3. SELECTED RESULTS OF ELECTRON-MICROPROBE ANALYSES OF THE KONDERITE-LIKE SULFIDE FROM THE PENIKAT COMPLEX

	Cu	Fe	Pb	Ni	Rh	Pd	Ir	Co	Pt	S	Total
1	9.89	2.25	7.82	0.74	29.34	4.61	14.99	0.33	0.58	28.32	98.87
2	9.86	2.35	7.31	0.72	30.17	4.55	15.02	0.46	0.44	28.67	99.55
3	10.21	2.35	7.18	0.70	29.65	4.44	14.95	0.44	0.49	28.59	99.00
4	9.58	2.57	6.91	0.66	31.29	4.38	14.46	0.47	0.73	28.81	99.86
5	9.62	2.84	6.64	0.64	31.70	3.82	14.15	0.43	0.69	29.28	99.81
6	9.63	3.11	5.58	0.62	31.66	3.24	14.61	0.43	0.76	29.15	98.79
7	10.05	3.18	5.23	0.60	32.03	3.16	14.73	0.42	0.71	29.32	99.43
8	9.90	3.00	5.18	0.59	31.87	3.09	14.60	0.52	0.86	29.42	99.03
9	9.94	3.14	4.28	0.48	32.50	2.57	14.93	0.39	0.72	29.72	98.67
10	10.29	3.21	4.22	0.47	32.21	2.68	14.93	0.48	0.68	29.65	98.82

The analytical results (in wt.%) are listed in order of decreasing content of Pb and refer to the rim-like grain (Kdr: shown by a white arrow), which forms part of the complexly zoned grain shown in Figure 1B. See the text for analytical conditions.

TABLE 4. ATOMIC PROPORTIONS OF THE KONDERITE-LIKE SULFIDE FROM THE PENIKAT COMPLEX

	Cu	Fe	Pb	Ni	Σ	Rh	Pd	Ir	Co	Pt	Σ	S
						7 apfu						
1	0.71	0.18	0.17	0.06	1.12	1.29	0.20	0.35	0.03	0.01	1.88	4.00
2	0.70	0.19	0.16	0.05	1.10	1.31	0.19	0.35	0.03	0.01	1.89	4.00
3	0.72	0.19	0.16	0.05	1.12	1.29	0.19	0.35	0.03	0.01	1.87	4.00
4	0.67	0.20	0.15	0.05	1.07	1.35	0.18	0.33	0.04	0.02	1.92	4.00
5	0.67	0.22	0.14	0.05	1.08	1.36	0.16	0.32	0.03	0.02	1.89	4.03
6	0.67	0.25	0.12	0.05	1.09	1.36	0.13	0.34	0.03	0.02	1.88	4.03
7	0.70	0.25	0.11	0.05	1.11	1.37	0.13	0.34	0.03	0.02	1.89	4.02
8	0.69	0.24	0.11	0.04	1.08	1.36	0.13	0.33	0.04	0.02	1.88	4.04
9	0.69	0.25	0.09	0.04	1.07	1.38	0.11	0.34	0.03	0.02	1.88	4.06
10	0.71	0.25	0.09	0.04	1.09	1.37	0.11	0.34	0.04	0.02	1.88	4.05
						28 apfu						
1	2.82	0.73	0.68	0.23	4.46	5.17	0.78	1.41	0.10	0.05	7.52	16.01
2	2.78	0.75	0.63	0.22	4.38	5.25	0.77	1.40	0.14	0.04	7.60	16.02
3	2.89	0.76	0.62	0.21	4.48	5.18	0.75	1.40	0.13	0.04	7.50	16.02
4	2.68	0.82	0.59	0.20	4.30	5.42	0.73	1.34	0.14	0.07	7.70	16.00
5	2.67	0.90	0.57	0.19	4.33	5.44	0.63	1.30	0.13	0.06	7.56	16.11
6	2.69	0.99	0.48	0.19	4.34	5.46	0.54	1.35	0.13	0.07	7.54	16.12
7	2.78	1.00	0.44	0.18	4.40	5.47	0.52	1.35	0.13	0.06	7.53	16.07
8	2.74	0.94	0.44	0.18	4.31	5.46	0.51	1.34	0.15	0.08	7.54	16.16
9	2.74	0.99	0.36	0.14	4.24	5.54	0.42	1.36	0.12	0.06	7.51	16.26
10	2.83	1.01	0.36	0.14	4.34	5.48	0.44	1.36	0.14	0.06	7.48	16.18

These values of atomic proportions are calculated on the basis of a total of 7 atoms per formula unit (*apfu*) and 28 *apfu* (*i.e.*, the thiospinel-type and konderite-type formula, respectively) and refer to the rim-like grain (Kdr: shown by a white arrow), which forms part of the complexly zoned grain shown in Figure 1B. See Table 3 for the analytical results (in wt.%).

TABLE 5. COMPOSITION OF PGE-RICH THIOSPINEL (CUPRORHODSITE – FERRORHODSITE – CUPROIRIDSITE SERIES) ASSOCIATED WITH THE KONDERITE-LIKE SULFIDE

	Cu	Fe	Ni	Rh	Ir	Co	Pt	S	Total
1	9.74	5.04	0.07	41.33	11.50	0.65	0.09	31.93	100.35
2	8.61	5.52	0.05	41.32	11.60	0.78	0.13	31.58	99.59
3	9.61	5.63	0.05	41.24	11.46	0.70	0.22	31.77	100.68
4	9.80	5.19	0.05	40.92	11.55	0.75	0.14	31.51	99.91
5	10.27	5.12	0.06	41.07	11.60	0.72	0.08	31.44	100.36
6	9.90	4.88	0.06	40.69	11.57	0.80	0.13	31.60	99.63
7	9.12	5.28	0.06	41.24	11.66	0.81	0.21	31.26	99.64
8	8.79	5.51	0.04	41.05	11.76	0.79	0.11	31.37	99.42
9	8.97	5.75	0.04	40.76	11.70	0.72	0.31	31.23	99.48
10	9.12	5.72	0.02	40.88	11.77	0.75	0.09	31.30	99.65
11	9.88	5.36	0.06	40.36	11.60	0.70	0.12	31.12	99.20
12	8.99	5.84	0.03	40.51	11.55	0.77	0.13	31.32	99.14
13	8.37	5.95	0.05	41.30	11.59	0.89	0.07	31.46	99.68
14	8.99	5.84	0.04	40.99	11.48	0.76	0.28	31.76	100.14
15	8.85	6.01	0.04	41.43	11.43	0.79	0.18	31.72	100.45

These electron-microprobe data (WDS: in wt.%) refer to a grain of cuprorhodsite – ferrorhodsite – cuproiridsite (labeled Cpr: Fig. 1A), which occurs in intergrowth with the konderite-like sulfide of Fe, Pb, Cu, Rh, Pd and Ir.

TABLE 6. ATOMIC PROPORTIONS OF THE PGE-RICH THIOSPINEL ASSOCIATED WITH THE KONDERITE-LIKE SULFIDE, PENIKAT COMPLEX

	Cu	Fe	Ni	Σ	Rh	Ir	Co	Pt	Σ	S
					7 apfu					
1	0.63	0.37	0.005	1.00	1.64	0.24	0.045	0.002	1.93	4.07
2	0.56	0.41	0.003	0.97	1.66	0.25	0.055	0.003	1.97	4.07
3	0.62	0.41	0.003	1.03	1.63	0.24	0.048	0.005	1.92	4.04
4	0.63	0.38	0.004	1.01	1.64	0.25	0.052	0.003	1.94	4.04
5	0.66	0.38	0.004	1.04	1.64	0.25	0.050	0.002	1.94	4.02
6	0.64	0.36	0.004	1.00	1.63	0.25	0.056	0.003	1.94	4.06
7	0.59	0.39	0.004	0.98	1.66	0.25	0.057	0.004	1.97	4.04
8	0.57	0.41	0.003	0.98	1.65	0.25	0.056	0.002	1.96	4.05
9	0.59	0.43	0.003	1.02	1.64	0.25	0.050	0.006	1.95	4.04
10	0.59	0.42	0.001	1.01	1.64	0.25	0.052	0.002	1.94	4.03
11	0.64	0.40	0.004	1.04	1.63	0.25	0.049	0.002	1.93	4.02
12	0.59	0.43	0.002	1.02	1.63	0.25	0.054	0.003	1.94	4.04
13	0.54	0.44	0.003	0.98	1.66	0.25	0.062	0.002	1.97	4.05
14	0.58	0.43	0.003	1.01	1.63	0.24	0.053	0.006	1.93	4.06
15	0.57	0.44	0.003	1.01	1.65	0.24	0.055	0.004	1.95	4.04

These values of atomic proportions refer to a grain of cuprorhodsite – ferrorhodsite – cuproiridsite (labeled Cpr: Fig. 1A), that occurs in intergrowth with the konderite-like sulfide of Fe, Pb, Cu, Rh, Pd and Ir. The corresponding analytical results (in wt.%) are listed in Table 5. The atomic proportions are calculated on the basis of a total of 7 atoms per formula unit.

$Fe_{0.40})_{\Sigma1.01}$ $(Rh_{1.65}Ir_{0.24}Co_{0.04})_{\Sigma1.93}$ $S_{4.05}$ is nearly identical to the formula of the large grain of Cpr, implying uniform conditions of crystallization. Interestingly, the Ir content in the average compositions of the coexisting PGE thiospinel and "Pb–(Fe)+Pd Kdr" (Fig. 1A) also is identical: 0.25 *apfu* (Σatoms = 7).

Element correlations in the "*Pb–(Fe)+Pd Kdr*"

Lead and Fe are negatively correlated in compositions of the "Pb–(Fe)+Pd Kdr", with *R* values of –0.95 and –0.94, for the LG (large grain) and RG (rim grain), respectively (Fig. 3A). Also, the correlation (Cu + Pb) *versus* Fe is strongly negative (*R* = –0.91: Fig. 3B). The Cu content correlates positively with Pb (Fig. 3C) and negatively with Fe (Fig. 3D) in the large grain of the "Pb–(Fe)+Pd Kdr". The Pb–Pd correlation is strongly positive (*R* = 0.95 and 0.99, for the LG and RG, respectively: Fig. 3E). In contrast, the Pb–Rh correlation is negative for both grains (Fig. 3F). Iron is negatively correlated with Pd (Fig. 4A), and correlates positively with Rh (Fig. 4B). The Rh content correlates negatively with Pd (Fig. 4C).

Contrasting behavior of Ni
and Co in the "*Pb–(Fe)+Pd Kdr*"

Nickel and Co are generally similar in their crystal-chemical behavior, and they substitute readily for each other in various minerals. These minor elements display a contrasting behavior in the "Pb–(Fe)+Pd Kdr", however. Nickel does not correlate with Co; also, Ni is negatively correlated with Fe (Fig. 5A), positively with Pb (Fig. 5B), negatively with Rh (Fig. 5C), and positively with Pd (Fig. 5D). In contrast, there is no statistically significant correlation of Co with any of these elements. On this basis, Ni and Co could be assigned to different structural sites in the thiospinel-type compound [AB_2X_4], *i.e.*, the Cu (*A*) and Rh (*B*) site, respectively, consistent with a synthetic $Cu_{1-x}Ni_xRh_2S_4$ thiospinel (Hart *et al.* 2000) and with Pt-rich carrollite [$Cu(Co,Pt)_2S_4$] ("dayingite": see Cabri 1981).

Evidence for nonstoichiometry in thiospinels

The PGE thiospinels and the associated "Pb–(Fe)+Pd Kdr" display a noticeable departure from the ideal AB_2X_4 stoichiometry. Typically, a minor excess in the atomic sum at the Cu (*A*) site is observed, coupled with a deficit at the Rh (*B*) site, and the content of S is slightly variable (Tables 1 to 4). These variations do not appear to be analytical artifacts; they are reproducible and consistent with experimental data from various thiospinel-type compounds. For example, cation-deficient thiospinels (Lotgering & Van der Steen 1971, Garg *et al.* 2001) and various defect thiospinels are known, such as synthetic $Cu_{1-x}[Ti_2]S_4$ with $0 < x \leq 0.93$ (James *et al.* 1989). A deficiency in sulfur is observed in the synthetic

thiospinel $CdCr_2S_4$, this being compensated for a partial reduction of Cr^{3+} to Cr^{2+} (Gibart *et al.* 1976). Also, evidence for S nonstoichiometry has been reported in synthetic $CuIr_2S_{4+x}$ (*i.e.*, cuproiridsite), with compositions having $x = –0.1$, 0.0, and 0.1 described by Somasundaram *et al.* (1997). In addition, the existence of synthetic $Cu_{1.5}Rh_{1.5}S_4$ (*e.g.*, Ohno *et al.* 1995) implies that an essential excess in Cu and deficit in Rh may be characteristic of cuprorhodsite and PGE thiospinels related to cuprorhodsite.

PGE thiospinels: crystal-chemical implications

The formal valences in the thiospinel–selenospinel systems are the following: $Cu^+_{1-x}Fe^{2+}_{2x-1}Fe^{3+}_{1-x}$ [Me^{3+}_2] X^{2-}_4 (for $0.5 \leq x \leq 1$; Me = Cr or Rh, and X = S or Se). For $0 < x \leq 0.5$, Fe is present only as Fe^{3+} in these chalcogenides (Riedel *et al.* 1981). For $x = 0$, the formal charges are Cu^+ [$Me^{3+}_{1+\delta}Me^{4+}_{1-\delta}$] $S^{2-}_{4-\delta}$ S^{-1}_δ [where S^{-1} is a hole in the valence band: Riedel *et al.* (1981), and references therein], for example, synthetic $Cu^+Cr^{3+}_2S^{2-}_3S^{-1}$ (Payer *et al.* 1990).

The mixed-valence state of Ir is characteristic of synthetic cuproiridsite: $Cu^+(Ir^{3+}Ir^{4+})S^{2-}_4$ (*e.g.*, Nagata *et al.* 1998). Synthetic end-member "$CuPt_2S_4$" (malanite), having the spinel-type structure, has not been reported, however. A monoclinic $Cu^+_2(Pt^{2+}Pt^{4+}_3)S_8$ phase (*P2/n*) is known instead, with a mixed-valence state of Pt ions (Gross & Jansen 1994). Barkov & Fleet (2004) suggest that a miscibility gap in the $CuRh_2S_4$–$CuIr_2S_4$– "$CuPt_2S_4$" system likely occurs close to "$CuPt_2S_4$". This suggestion is consistent with the fact that no end-member malanite (either natural or synthetic) is known, although very wide ranges of mutual solid-solutions have been documented among the natural PGE thiospinels (*e.g.,* Cabri *et al.* 1996).

Although Cu is characterized as being monovalent in various thiospinel-type compounds, the Cu-excess character of synthetic $Cu_{1.5}Rh_{1.5}S_4$ (*e.g.*, Ohno *et al.* 1995) may imply the presence of Cu^{2+}. Furukawa *et al.* (1995) proposed that all Cu could be divalent in a related thiospinel phase: $Cu^{2+}[Cu^{2+}_{0.5}Co^{3+}_{1.5}]S_{4-\delta}$. The minor excess in Cu over that required for full occupancy of the *A* site, which is observed in the PGE thiospinels related to cuprorhodsite, is consistent with a limited incorporation of Cu^{2+} at the Rh (*B*) site in the spinel structure.

In various solid solutions of PGE-rich thiospinels, Pt appears to be dominantly present as Pt^{4+}, whereas Ir may occur as Ir^{3+} and Ir^{4+}. The compositions of PGE thiospinels reported by Rudashevskii *et al.* (1985) imply that the Ir is strongly dominated by Ir^{3+}. In contrast, nearly all Ir appears to occur as Ir^{4+} in the PGE thiospinels from the Penikat complex, consistent with the observed association of these thiospinels with abundant Pd–Pb oxide (Barkov *et al.* 1999, 2000). Thus, an elevated fugacity of oxygen, $f(O_2)$, in the environment at Kirakkajuppura could be important in controlling the

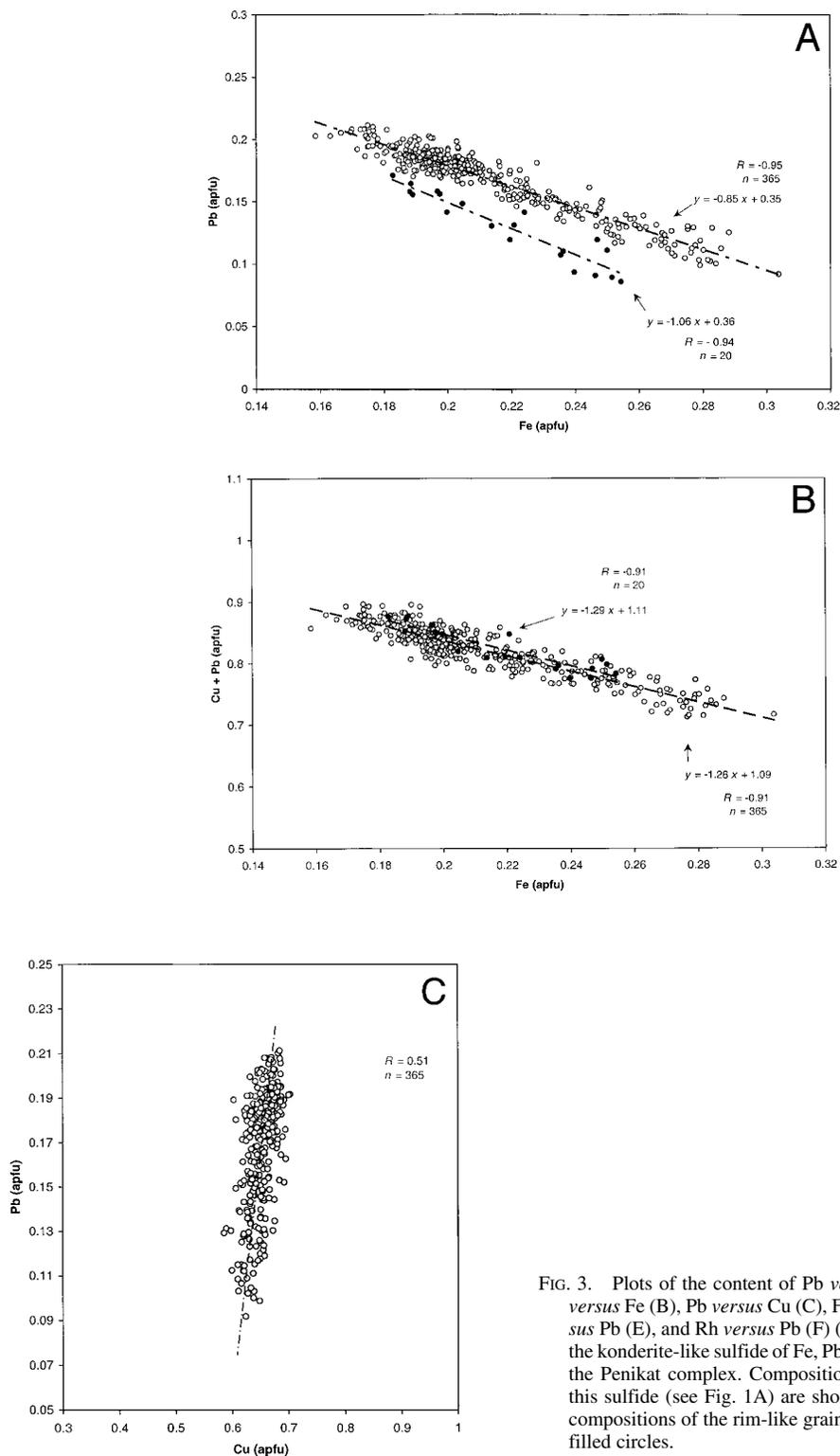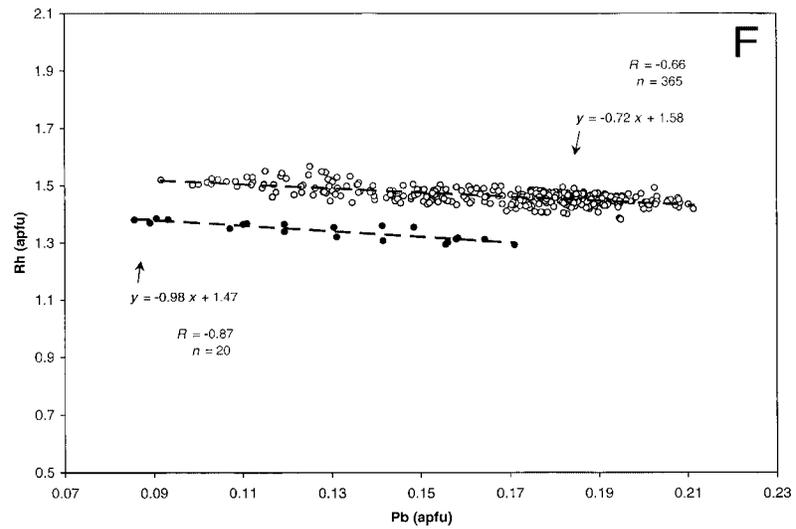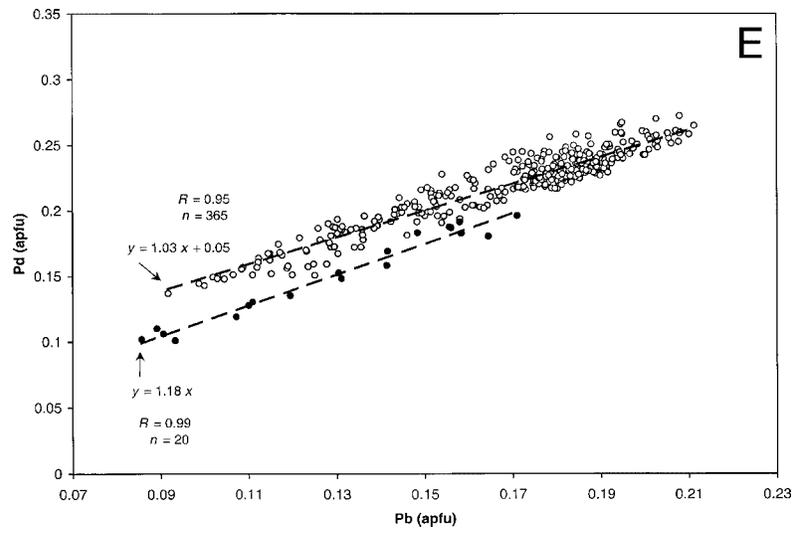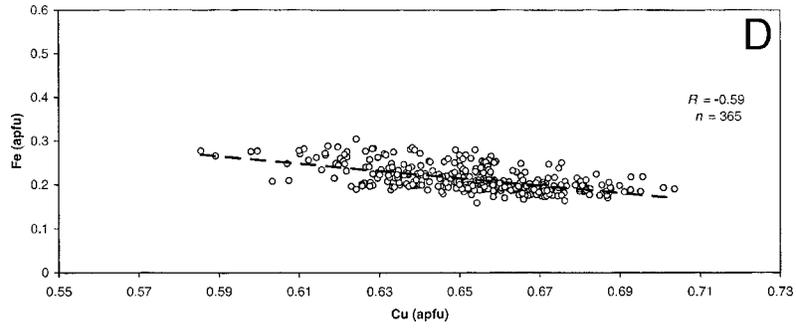FIG. 3. Plots of the content of Pb *versus* Fe (A), (Cu + Pb) *versus* Fe (B), Pb *versus* Cu (C), Fe *versus* Cu (D), Pd *versus* Pb (E), and Rh *versus* Pb (F) (in *apfu*: Σatoms = 7) for the konderite-like sulfide of Fe, Pb, Cu, Rh, Pd, and Ir from the Penikat complex. Compositions of the large grain of this sulfide (see Fig. 1A) are shown by open circles, and compositions of the rim-like grain (Fig. 1B) are shown by filled circles.
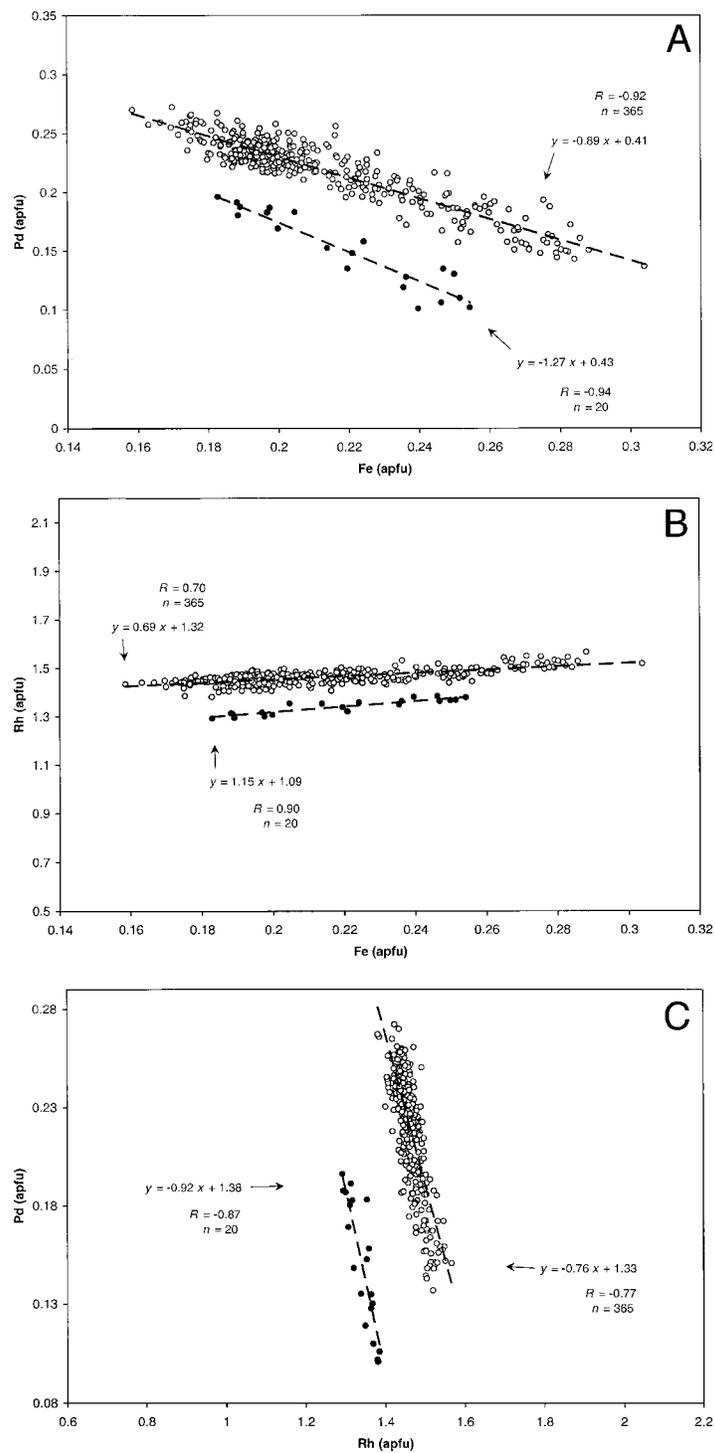
D

R = -0.59
n = 365

Fe (apfu)

Cu (apfu)

E

R = 0.95
n = 365

y = 1.03 x + 0.05

Pd (apfu)

y = 1.18 x

R = 0.99
n = 20

Pb (apfu)

F

R = -0.66
n = 365

y = -0.72 x + 1.58

Rh (apfu)

y = -0.98 x + 1.47

R = -0.87
n = 20

Pb (apfu)

FIG. 4. Plots of the content of Pd *versus* Fe (A), Rh *versus* Fe (B), and Pd *versus* Rh (C) (in *apfu*: Σatoms = 7) for the konderite-like sulfide of Fe, Pb, Cu, Rh, Pd, and Ir from the Penikat complex. See Figure 3 for the key to symbols.
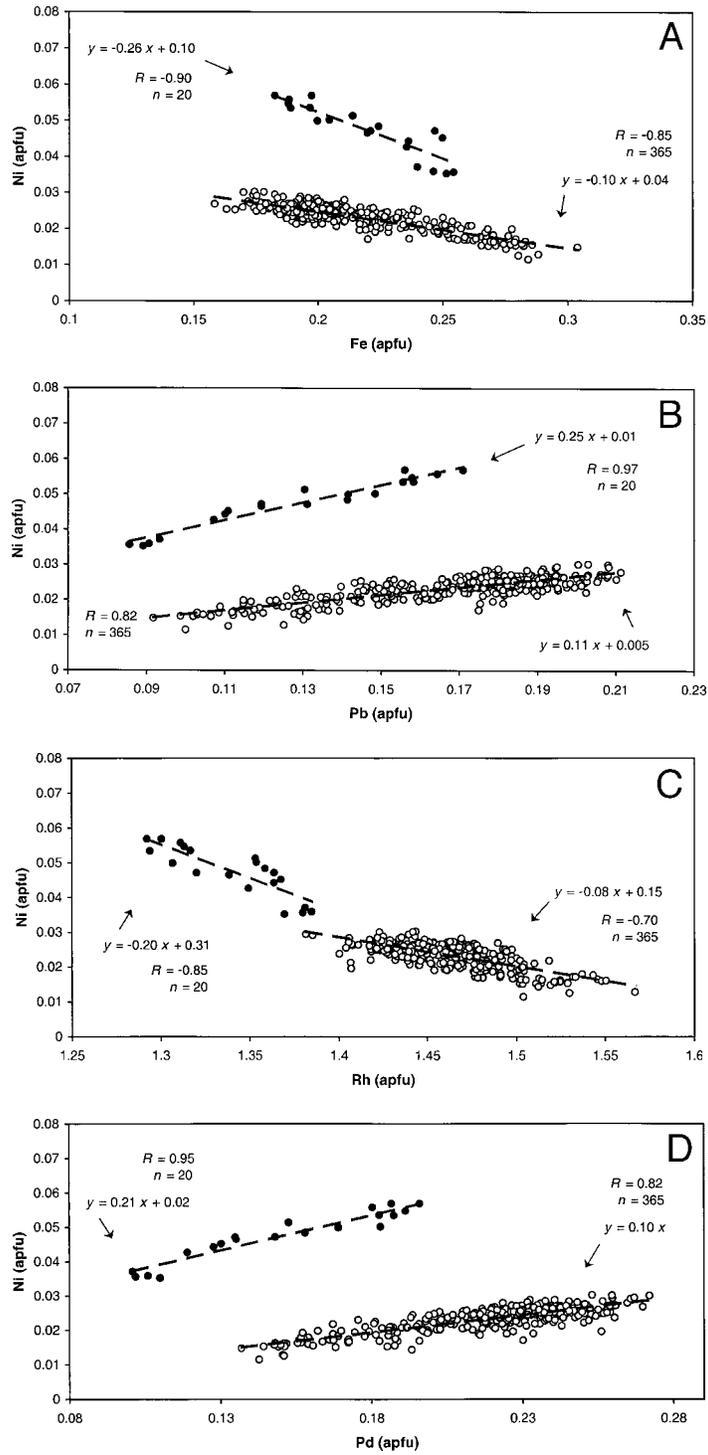
FIG. 5. Plots of the content of Ni *versus* Fe (A), Ni *versus* Pb (B), Ni *versus* Rh (C), and Ni *versus* Pd (D) (in *apfu*: Σatoms = 7) for the konderite-like sulfide of Fe, Pb, Cu, Rh, Pd, and Ir from the Penikat complex. See Figure 3 for the key to symbols.

valence of Ir in the PGE-bearing thiospinels. In addition, the valence states of the elements present in thiospinels may also depend on other factors, such as the temperature regime or S activity (*e.g.*, Botsan *et al.* 1989, Juszczyk & Gogolowicz 1991).

Mechanism of charge compensation in PGE thiospinels

On the basis of the findings of Riedel *et al.* (1981), we assume that the Cpr at Kirakkajuppura contains Cu^+, Rh^{3+}, and Fe^{3+}, being essentially devoid of Fe^{2+}; also, Ir likely occurs as Ir^{4+} (Barkov *et al.* 2000). These valences are consistent with the requirements of electroneutrality and with the average formulae $[(Cu_{0.60–0.6}Fe_{0.40–0.41})_{\Sigma1.01}(Rh_{1.64–1.65}Ir_{0.24–0.25}Co_{0.04–0.05})_{\Sigma1.93–1.94}S_{4.05}]$ of the PGE thiospinels intergrown with the "Pb–(Fe)+Pd Kdr" grains (Figs. 1A, C). Also, they are consistent with the scheme of coupled charge-balance substitution $[{}^{A}Cu^+ + 2\ {}^{B}Pt^{4+}(+2\ Ir^{4+}) = {}^{A}Fe^{3+} + 2\ {}^{B}Rh^{3+}]$ formulated for the PGE thiospinels in Barkov *et al.* (2000). It is noteworthy that extensive coupled substitutions are uncharacteristic of sulfide minerals, with the first example being reported in renierite (Bernstein 1986).

Comparison with "xingzhongite"

The data reported on "xingzhongite" in the literature are somewhat muddled. It was first reported as being cubic (Ir,Cu,Rh,Pb)S with a value of the cell parameter *a* equal to 8.72 Å (abstracted by Chao & Cabri 1976), then with a value of 10.10 Å (abstracted by Cabri 1980). A revised description was subsequently reported, with a Pb-dominant composition cast in a thiospinel-type formula: $(Pb_{0.37}Cu_{0.35}Fe_{0.17})_{\Sigma0.89}\ (Ir_{1.33}Rh_{0.41}Pt_{0.29})_{\Sigma2.03}S_4$ and *a* equal to 9.97 Å (abstracted by Chao 1984). Mandarino (1999) listed "xingzhongite" as a valid species with the general formula $(Pb,Cu,Fe)(Ir,Pt,Rh)_2S_4$, as do, tentatively, Strunz & Nickel (2001, p. 94). The fact remains that "xingzhongite" still is not an IMA-approved species. Cabri (2002) dismissed it as plumboan cuproiridsite. There is also a possibility that "xingzhongite" is in fact inaglyite (*i.e.*, the Ir-dominant analogue of konderite: Rudashevskii *et al.* 1984a). The composition reported in the abstract by Chao (1984) may be satisfactorily recalculated into a konderite–(inaglyite)-type formula: $Pb_{1.00}\ (Cu_{1.43}Fe_{0.68}Pb_{0.48})_{\Sigma2.59}(Ir_{5.41}Rh_{1.67}Pt_{1.18})_{\Sigma8.26}\ S_{16.15}$ (this study); the XRD patterns of the thiospinel and thiospinel-derivative PGM are generally similar, being distinct only in the presence of a few superstructure lines (Rudashevskii *et al.* 1984a, b). No further comparison is possible without improved documentation on the Chinese material.

A structural formula for konderite

We note that the mean composition of konderite (Rudashevskii *et al.* 1984b) approximately corresponds to the generalized formula $PbCu_3Rh_3Ir_2Pt_3S_{16}$. Thus, the following structural formula, shown with "common" formal valences for the participating elements, consistent with a thiospinel-derivative structure, may be suggested for konderite from the type locality: $Pb^{2+}Cu^+_3[Rh^{3+}_3Ir^{3+}_2Pt^{4+}_3]S^{2-}_{16}$.

Mechanism of charge compensation in the "Pb–(Fe)+Pd Kdr"

The PGE thiospinel associated with the "Pb–(Fe)+Pd Kdr" at Kirakkajuppura is assumed to contain Cu^+, Rh^{3+}, Ir^{4+} and Fe^{3+}, consistent with the generalized structural formula of Riedel *et al.* (1981). These formal valences and the presence of Pb^{2+} (*cf.*, konderite from Kondyor) and Pd^{2+} could be accommodated in a konderite-like formula consistent with the average compositions of the konderite-like sulfide from the Penikat complex. The observed variations and element-correlations (Figs. 3A to 5D) are indicative of a Pb-for-Fe substitution, which is controlled by Pd-for-Rh substitution. These substitutions are evident from the compositional trends of both the observed textural forms of the "Pb–(Fe)+Pd Kdr" (Figs. 1A, B), which are also internally consistent with each other (Figs. 3A to 5D). However, in the large grain of "Pb–(Fe)+Pd Kdr", Cu displays a weak positive correlation with Pb (Fig. 3C) and is negatively correlated with Fe (Fig. 3D). Thus, Cu is likely partially involved in the charge-balance substitution operating in the large grain, in accordance with the following approximate scheme of charge-balance substitution: $[Cu^+ + 2\ (Pb + Ni)^{2+}] + 2\ Pd^{2+} = 2\ Fe^{3+} + Rh^{3+}]$. In contrast, there is no evidence for the involvement of Cu in charge-balancing substitution in the rim-like grain. Instead, Ni could be essential here, consistent with the Ni-rich composition of this grain and its covariance with Fe, Pb, Rh, and Pd (Figs. 5A–D). Note that variations in S could be also essential in maintaining charge balance, as is suggested by the observed negative correlations of S with Pb^{2+} and Pd^{2+}, and positive correlations of S with Fe^{3+} and Rh^{3+}.

Genetic implications

The konderite-like sulfide is a newly reported Pb-rich species of PGM observed in the Kirakkajuppura PGE deposit. The occurrence of the PGE thiospinels and konderite-like minerals in this deposit hosted by a layered intrusion is very unusual, because these PGM are commonly associated with various Uralian–Alaskan-type complexes or related placers (*e.g.*, Rudashevskii *et al.* 1984a, b, 1985, 1998, Cabri *et al.* 1996). We suggest that the appearance of these minerals at Kirakkajuppura is related to the anomalously S-poor character of this deposit, as is the rule in Uralian–Alaskan-type rocks. Our generalization is consistent with the occurrence of another thiospinel-like phase $[Cu^+_2(Ni,Co)^{2+}Pt^{4+}_3S_8]$, akin to synthetic monoclinic $Cu^+_2Pt^{2+}Pt^{4+}_3S_8$ (Gross & Jansen 1994), in a S-poor chromitite in the Imandra lay-

ered complex, Kola Peninsula, northwestern Russia (Barkov & Fleet 2004). The occurrence of laflammeite ($Pd_3Pb_2S_2$), a unique parkerite-type sulfide [*i.e.*, S-poor with a (Pd + Pb):S of 2.5], in association with the "Pb–(Fe)+Pd Kdr" and various PGE thiospinels at Kirakkajuppura, is consistent with the S-poor character of the environment (Barkov *et al.* 2002).

The relative abundance of various Pb-rich PGM (zvyagintsevite, an unnamed Pd–Pb oxide, laflammeite, Pb-rich keithconnite and the konderite-like sulfide) give the Kirakkajuppura PGE deposit its "anomalous" characteristic. Magmatic contamination from footwall rocks, which are mainly late Archean granitic rocks, could explain the observed enrichment in Pb; the location of this deposit is indeed relatively close to country rocks. Alternatively, the Pb could be externally derived, transported and introduced to the zone of mineralization by a mobile hydrothermal fluid(s). The PGE-mineralized rocks at Kirakkajuppura have been overprinted by an episode of extensive hydrothermal–metasomatic alteration, as the PGM occur in intimate association with hydrous silicates (Barkov *et al.* 1999). The presence of the unnamed Pb–V oxide [$Pb_4O(VO_4)_2$] and late-stage micro-aggregates of zvyagintsevite, which are controlled by microfractures and cleavages in hydrous silicates, would be consistent with this model. Lead is mobile in a hydrous fluid, consistent with the occurrence of a penfieldite-like phase [$Pb_2Cl_3(OH)$] in a close association with PGM in the Merensky Reef, Bushveld complex (Barkov *et al.* 2001). In a third possibility, the igneous rocks of the Penikat complex could be the primary source of Pb. This complex likely crystallized from a boninite-like parental magma (Alapieti & Halkoaho 1995, and references therein), which could have been relatively enriched in Pb, PGE, H_2O, and other volatile species. Presumably, magmatic crystallization would lead to a further enrichment in Pb in those units located near the marginal series of the complex. The Pb, along with the PGE, could have been subsequently mobilized by a hydrothermal fluid(s), giving rise to various species of PGM rich in Pb in the mineralized zone at a late stage of postmagmatic crystallization of the complex.

The "Pb–(Fe)+Pd Kdr" likely formed from microvolumes of a late-stage liquid or fluid. The associated PGE thiospinels are essentially devoid of Pb, even though they commonly contain abundant inclusions of zvyagintsevite. The "Pb–(Fe)+Pd Kdr" may have developed through exsolution from the PGE thiospinel (Cpr; Fig. 1A); however, the large grain of the "Pb–(Fe)+Pd Kdr" may also have formed by direct crystallization nearly simultaneously with the associated PGE thiospinel (Fig.1A). Interestingly, these two phases clearly reached equilibrium in the distribution of Ir, as they both contain equal amounts of Ir (0.25 *apfu*: Σatoms = 7). In contrast, all the Pb was selectively partitioned into the "Pb–(Fe)+Pd Kdr"; the incorporation of Pb is here clearly controlled by the presence of Pd (Fig. 3E). This feature is consistent with the Pb-poor compositions of the PGE thiospinels at Kirakkajuppura, and implies the existence of crystal-chemical constraints for the incorporation of Pb in PGE thiospinels.

The rim-like grain of the "Pb–(Fe)+Pd Kdr" clearly formed after the associated PGM of the laurite–erlichmanite and irarsite–hollingworthite series (Fig. 1B). Inaglyite, the Ir-rich analogue of konderite, also formed as a rim around laurite in the Inagli alkali-ultramafic complex, northeastern Russia (Rudashevskii *et al.* 1984a). Interestingly, a decrease in temperature during crystallization of this polymineralic grain of PGM (Fig. 1B) is indicated by the increase in minor amounts of Fe in the Ru–Os–Ir–(Rh) disulfides and sulfarsenides toward the grain margin (Barkov *et al.* 2004). Presumably, Pb was incompatible during the crystallization of the laurite–erlichmanite and irarsite–hollingworthite, giving rise to the "Pb–(Fe)+Pd Kdr" at a low temperature, at the final stage of crystallization of this complexly zoned grain of PGM.

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