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IRIDIUM, RHODIUM, AND PLATINUM SULFIDES IN CHROMITITES FROM THE ULTRAMAFIC MASSIFS OF FINERO, ITALY, AND OJÉN, SPAIN

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ABSTRACT

Cuprorhodsite, cuproiridsite, malanite, and other unknown sulfides of Ir, Rh, and Pt occurring as primary inclusions (up to about 12 μm) in fresh chromite of chromitites from the ultramafic massifs of Finero (Western Alps, Italy) and Ojén (Betic Cordillera, Spain) have been investigated by electron-microprobe analysis. Compositions obtained for cuprorhodsite, cuproiridsite, and malanite, combined with data from the literature, confirm the existence of extensive solid-solution in the system $CuRh_2S_4$–$CuIr_2S_4$–$CuPt_2S_4$, although Pt-rich representatives close to pure malanite have not yet been found in nature. Among the other minerals, an (Ir,Rh)-rich Ni–Fe–Cu sulfide (unknown #1) is the most common. Compositions documented here and from the literature are consistent with the stoichiometry $(Ni,Fe,Cu)_2(Ir,Rh)S_3$, although it is still an open question whether these compositions represent an independent mineral species or pertain to PGE-rich pyrrhotite and pentlandite. The other sulfides are: $(Ir,Rh)_3(Ni,Fe,Cu)_2S_5$, probably xingzhongite, $(Rh,Cu)_3S_2$ (unknown #2), and a Pt,Rh,Ir,Cu sulfide (unknown #3). Cuprorhodsite, cuproiridsite, malanite, and a (Ir,Rh)-rich Ni–Fe–Cu sulfide similar to unknown #1 have commonly been reported from placer deposits, mostly derived from Alaskan-type complexes or from other uncertain source-rocks. More rarely, they have been described *in situ* from ophiolitic chromitites. The occurrences of Finero and Ojén indicate that these minerals can be found *in situ* also within chromitite from the lithospheric mantle underneath the continental crust.

Keywords: cuprorhodsite, cuproiridsite, malanite, Ir–Rh sulfides, Finero, Western Alps, Italy, Ojén, Betic Cordillera, Spain.

SOMMAIRE

Nous avons établi la présence de cuprorhodsite, cupro-iridsite, malanite et autres sulfures méconnus d'Ir, de Rh et de Pt, comme inclusions primaires (jusqu'à 12 μm de taille) dans la chromite de chromitite des massifs ultramafiques de Finero (Alpes occidentales, Italie) et d'Ojén (Cordillère bétique, Espagne). Les compositions de cuprorhodsite, de cupro-iridsite, et de malanite, obtenues avec une microsonde électronique et présentées avec les données dans la littérature, confirment l'existence d'une solution solide étendue dans le système $CuRh_2S_4$–$CuIr_2S_4$–$CuPt_2S_4$, quoique les exemples platinifères proches du pôle malinite n'ont pas encore été repérés comme minéraux. Parmi les autres minéraux, le sulfure de Ni–Fe–Cu riche en Ir et en Rh (inconnu #1) est le plus répandu. Nos compositions et celles dans la littérature concordent avec une stoechiométrie $(Ni,Fe,Cu)_2(Ir,Rh)S_3$, quoiqu'il ne soit pas encore clair s'il s'agit d'une espèce minéralogique distincte ou d'une pyrrhotite ou d'une pentlandite enrichie en éléments du groupe du platine. Les autre sulfures sont: $(Ir,Rh)_3(Ni,Fe,Cu)_2S_5$, probablement xingzhongite, $(Rh,Cu)_3S_2$ (inconnu #2), et un sulfure de Pt, Rh, Ir et Cu (inconnu #3). Cuprorhodsite, cupro-iridsite, malanite, et sulfure de Ni–Fe–Cu enrichi en Ir et Rh semblable à l'inconnu #1 sont assez répandus dans les graviers alluvionnaires dérivés de complexes dits de type Alaska, ou bien d'autres sources quelconques moins bien caractérisées. Il est plus rare de les rencontrer *in situ* dans la chromitite des massifs ophiolitiques. Leur présence dans les massifs de Finero et d'Ojén démontre que ces minéraux se trouvent aussi *in situ* dans la chromitite de la couche lithosphérique du manteau en dessous de la croûte continentale.

(Traduit par la Rédaction)

Mots-clés: cuprorhodsite, cupro-iridsite, malanite, sulfures d'Ir et de Rh, massif de Finero, Alpes occidentales, Italie, massif d'Ojén, Cordillère bétique, Espagne.

INTRODUCTION

Preliminary reports of platinum-group minerals (PGM) from chromitites in the ultramafic massifs of Finero (Western Alps, Italy) and Ojén (Betic Cordillera, Spain) have been given by Ferrario & Garuti (1990) and Torres-Ruiz *et al.* (1993), respectively. In the course of both investigations, some grains of sulfides containing Ir, Rh, and Pt as the major platinum-group elements (PGE), as well as the base metals (BM) Ni, Cu, and Fe, were occasionally encountered included in fresh chromite, although they were only qualitatively identified in most cases. Further examination of chromitite samples from both massifs reveals a more extensive occurrence of these PGM, and a much greater number of mineral species than previously supposed. The present work reports the results of a systematic electron-microprobe investigation of a considerable number of grains, which allowed the chemical characterization of the PGM, and in some cases the definition of the pertinent mineral species. Some of the identified minerals (cuprorhodsite, cuproiridsite, malanite) correspond to PGM already known in the literature, whereas some others probably are unknown phases. Most of the PGM described represent the first documented occurrences in Italy and Spain.

GEOLOGICAL SETTING AND OCCURRENCE

The Finero and Ojén ultramafic massifs belong to two distinct suites of Alpine-type peridotite bodies located respectively in the Western Alps (Italy) and in the Betic Cordillera (southern Spain). The massifs are considered to be slices of lithospheric mantle emplaced into continental crust (Nicolas & Jackson 1972), and to have equilibrated under granulite-facies conditions. Both ultramafic massifs are characterized by a roughly symmetrical zonation from the core outward (Fig. 1), although with remarkable differences in lithological association: phlogopite peridotite, amphibole-rich pyroxenite and gabbro, and amphibole peridotite at Finero, and plagioclase lherzolite, spinel lherzolite, and garnet lherzolite at Ojén. The bodies of chromitite are small, extending over a few square meters, and in both massifs they occur in the form of schlieren and pods sporadically distributed in the core zones of phlogopite peridotite (Finero) and plagioclase lherzolite (Ojén). The structural and compositional characteristics are similar to those of podiform chromitite, although they formed in the subcontinental mantle, thus under geodynamic conditions different from those of ophiolite complexes. Petrographic and compositional details of the chromitite bodies can be found in Ferrario & Garuti (1990) and Gervilla & Leblanc (1990) for Finero and Ojén, respectively.

The Ir–Rh–Pt sulfides that are object of the present investigation were found at the localities of Alpe Polunia, Rio Creves, and Torrente Provola (Finero), and Arroyo de los Caballos (Ojén). Analytical data for the same minerals from unspecified localities in the Finero massif, taken from Table 3 in Ferrario & Garuti (1990), also are discussed. The Ir–Rh–Pt sulfides are part of a complex association of PGM comprising laurite, irarsite, native Ir and Pt- and Rh-bearing alloys, at Finero (Ferrario & Garuti 1990), and laurite, Ir–Ru–Os sulfarsenides, sperrylite, and unidentified Pd-compounds with S, Bi and As, at Ojén (Torres-Ruiz *et al.* 1993). At both localities, the Ir–Rh–Pt sulfides occur included in fresh chromite, generally far from fractures, and are interpreted as having been trapped in the chromite at the time of its crystallization. All grains are very small, the longest axis ranging from 2 to about 12 μm. Most have an anhedral shape and occur intergrown with laurite, irarsite, and Ni–Fe–Cu sulfides such as millerite, pentlandite, and chalcopyrite. Single-phase grains are rare, and were observed only at Finero. Such grains are the largest in the suite, and roughly polygonal in shape, suggesting free growth in an unconstrained environment.

ANALYTICAL TECHNIQUES

The PGM grains were investigated *in situ*, in polished sections by reflected-light microscopy and by electron-microprobe analysis by energy-dispersion and wavelength-dispersion spectrometry (EDS and WDS, respectively). Owing to the small size of the grains, optical properties observed using oil immersion were limited to color and anisotropy. An estimate of the reflectance has been given by comparison with associated PGM and common sulfides.

Back-scattered electron (BSE) images of grains were acquired at the University of Granada using a

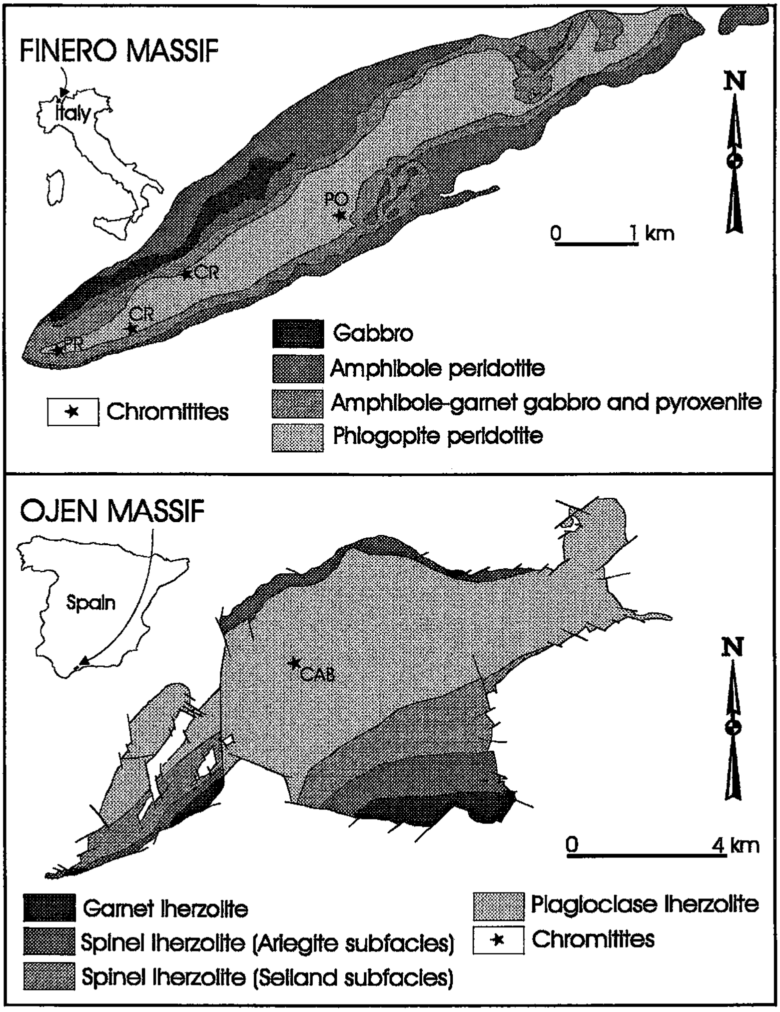

FIG. 1. Geological sketch of the Finero and Ojén ultramafic massifs showing zonation in lithology, and location of the chromitite hosting the PGM investigated. PO: Alpe Polunia, CR: Rio Creves, PR: Torrente Provola, CAB: Arroyo de los Caballos.

Cameca SX50 electron microprobe operated at an accelerating voltage of 20 kV with a beam current of 20–50 nA. Quantitative WDS analyses were carried out at the University of Modena using an ARL–SEMQ instrument operated at an accelerating voltage of 27 kV, and a beam current of 20 nA, with a beam diameter of about 1 µm. The X-ray lines monitored were as follows: $K\alpha$ for S, Cr, Fe, Ni, and Cu; $L\alpha$ for Ir, Ru, Rh, Pt, Pd, and As, and $M\alpha$ for Os. Corrections were made for the observed interferences RuRh, RuAs, IrCu, RhPd. The standards natural chromite (Cr), synthetic NiAs, FeS_2, $CuFeS_2$ (Ni, Fe, Cu, S, and As), and pure metals (PGE) were used. Because of the small size of grains, variable amounts of Cr and Fe were observed in all analytical runs as the result of secondary fluorescence or direct excitation of the host chromite; therefore, the analytical results have been recalculated subtracting all the Cr and a proportional amount of Fe, as deduced from the Cr–Fe ratio of the host spinel. A further correction was applied to the analyses of some small grains intergrown with pentlandite by subtracting amounts of Ni, Fe, and S as determined by the composition of pentlandite.

RESULTS

Results of electron-microprobe analyses of the minerals are listed in Tables 1 and 2. All data, together with eight compositions of Ir–Rh–Pt–Cu sulfides from Finero (Ferrario & Garuti 1990, Table 3) have been plotted in the system S – (Fe+Ni+Cu) – (Ir+Rh+Pt) (Fig. 2). They define two main groups clustering around the thiospinel (X_3S_4) and the monosulfide (XS) stoichiometries. One grain is close to X_2S_3, whereas two others match the metal-excess stoichiometry X_3S_2 perfectly.

The cuprorhodsite – cuproiridsite – malanite series

The thiospinel PGM have general formula $(Ir,Rh,Pt)_2(Cu,Fe)S_4$ with Cu > Fe, and very minor amounts of Ni, usually not exceeding 0.4 at.%. Depending on the dominant PGE, they can be attributed to the cuprorhodsite-, cuproiridsite-, and malanite-series minerals.

Cuprorhodsite (ideally $CuRh_2S_4$) was found at Finero as a polygonal, single-phase grain included in unfractured chromite (Fig. 3A). The mineral is isotropic and white-grey. Although qualitatively

TABLE 1. COMPOSITIONS OF CUPRORHODSITE, CUPROIRIDSITE AND MALANITE FROM FINERO AND OJEN CHROMITITES

	Cr	Fe	Ni	Cu	Os	Ir	Ru	Rh	Pt	Pd	S	Total
Weight percent (row data)												
Cuprorhodsite												
CR1367–1a–1	1.60	5.34	0.26	8.98	0.06	17.47	0.00	32.38	2.49	2.67	27.84	99.09
CR1367–1a–2	2.37	5.42	0.28	8.77	0.05	16.94	0.00	33.06	2.45	3.62	26.23	99.19
CR1367–1a–3	1.84	5.41	0.38	9.00	0.00	17.32	0.00	34.65	2.52	4.16	28.05	103.33
CR1367–1a–4	1.93	5.46	0.29	8.80	0.03	16.94	0.02	33.51	2.41	4.34	28.41	102.14
Cuproiridsite												
CR1367–1b–1	2.54	2.04	0.30	10.92	0.08	33.63	0.00	15.72	10.03	1.37	24.40	101.03
CR1367–1b–3	2.47	2.05	0.31	10.99	0.09	33.41	0.04	15.94	9.93	2.11	23.66	101.00
PO1355–4–2	8.88	3.83	0.24	8.49	0.00	46.85	0.35	8.51	0.00	0.81	19.30	97.26
PO1355–4–4	4.26	3.13	0.29	8.12	0.00	50.98	0.57	8.62	0.00	0.21	22.33	98.51
Malanite												
CAB1–2–2	4.51	4.49	3.58	10.27	0.04	6.44	0.18	12.33	34.60	1.76	24.83	103.03
CAB3–15–2	4.30	3.46	3.02	10.19	0.16	13.79	0.03	9.33	34.38	1.47	24.32	104.45
Corrected weight percent (data corrected for the chromite and pentlandite (*) matrix effect												
Cuprorhodsite												
CR1367–1a–1		4.54	0.26	8.98	0.06	17.47	0.00	32.39	2.49	2.67	27.84	96.70
CR1367–1a–2		4.24	0.28	8.77	0.05	16.94	0.00	33.06	2.45	3.62	26.23	95.64
CR1367–1a–3		4.49	0.38	9.00	0.00	17.32	0.00	34.65	2.52	4.16	28.04	100.56
CR1367–1a–4		4.50	0.29	8.80	0.03	16.94	0.02	33.51	2.41	4.34	28.41	99.25
Cuproiridsite												
CR1367–1b–1		0.78	0.30	10.91	0.08	33.64	0.00	15.72	10.03	1.37	24.40	97.23
CR1367–1b–3		0.82	0.31	10.99	0.09	33.41	0.04	15.94	9.93	2.11	23.66	97.30
PO1355–4–2		0.00	0.24	8.49	0.00	46.86	0.35	8.51	0.00	0.81	19.30	84.56
PO1355–4–4		1.13	0.29	8.12	0.00	50.99	0.57	8.62	0.00	0.21	22.33	92.26
Malanite												
CAB1–2–2 *		0.59	0.00	10.27	0.04	6.44	0.18	12.33	34.60	1.76	22.22	88.43
CAB3–15–2 *		0.00	0.26	10.19	0.16	13.79	0.03	9.33	34.38	1.47	22.34	91.95
Atomic percent (calculated from corrected data)												
Cuprorhodsite												
CR1367–1a–1		5.282	0.282	9.184	0.020	5.906	0.000	20.448	0.831	1.633	56.413	
CR1367–1a–2		5.088	0.320	9.243	0.018	5.903	0.000	21.516	0.840	2.279	54.794	
CR1367–1a–3		5.087	0.411	8.952	0.000	5.694	0.000	21.284	0.817	2.470	55.284	
CR1367–1a–4		5.109	0.313	8.783	0.011	5.587	0.013	20.647	0.783	2.586	56.170	
Cuproiridsite												
CR1367–1b–1		1.040	0.384	12.776	0.031	13.016	0.000	11.363	3.825	0.958	56.608	
CR1367–1b–3		1.103	0.393	12.997	0.034	13.059	0.030	11.638	3.826	1.491	55.430	
PO1355–4–2		0.000	0.386	12.402	0.000	22.628	0.321	7.677	0.000	0.704	55.881	
PO1355–4–4		1.670	0.403	10.600	0.000	21.995	0.468	6.944	0.000	0.163	57.756	
Malanite												
CAB1–2–2		0.870	0.000	13.309	0.018	2.759	0.143	9.864	14.604	1.361	57.072	
CAB3–15–2		0.000	0.366	13.193	0.070	5.903	0.025	7.461	14.507	1.138	57.338	

Samples: CR1367–1a–1 to 1a–4 refer to Figure 3C, CR1367–1b–1 and 1b–3, to Figure 3B, PO1355–4–2 and 4–4 to Figure 4B, CAB1–2–2 to Figure 5A, and CAB3–15–2 to Figure 5C. Prefixes: CR: Rio Creves, PO: Alpe Polunia (Finero), CAB: Arroyo de los Caballos (Ojén).

estimated, reflectance appears to be slightly lower than that of laurite. Four points analyzed (Fig. 3C, anal. CR1367–1a–1 to 1a–4, Table 1) indicate that the grain is nearly homogeneous, corresponding to $(Cu_{0.63}Fe_{0.36}Ni_{0.02})_{\Sigma 1.01}(Rh_{1.47}Ir_{0.40}Pd_{0.16}Pt_{0.06})_{\Sigma 2.09}S_{3.90}$ on average. The amount of Fe substituting for Cu, after correction for the fluorescence effect due to chromite, was considerable, being the highest observed in the group.

Two grains of cuproiridsite from Finero were analyzed (anal. CR1367–1b–1, 1b–3 and PO1355–4–2, 4–4, Table 1). Both grains occur as part of composite inclusions. One is associated with an unknown (Ir,Rh)-rich Ni–Fe–Cu sulfide (Figs. 3A,B), and the other with laurite and minor irarsite (Fig. 4B). The mineral is isotropic, but exhibits different color and reflectance in each case, possibly related to differences in composition. Grain CR1367–1b is optically very similar to cuprorhodsite. Actually, its average composition is $(Cu_{0.9}Fe_{0.08}Ni_{0.03})_{\Sigma 1.01}(Ir_{0.91}Rh_{0.81}Pt_{0.27}Pd_{0.09})_{\Sigma 2.08}S_{3.92}$, and approaches the cuprorhodsite field. In contrast, grain PO1355–4–2 is greenish grey and remarkably less reflective than laurite. The analyses indicate that the mineral is richer in Ir, and does not contain any Pt,

TABLE 2. COMPOSITIONS OF UNKNOWN Ir, Rh, AND Pt SULFIDES FROM FINERO AND OJEN CHROMITITES

	Cr	Fe	Ni	Cu	Os	Ir	Ru	Rh	Pt	Pd	S	As	Total
Weight percent (row data)													
Unknown # 1													
CAB1–1	3.72	10.85	18.30	5.54	0.21	21.22	0.49	13.17	1.72	0.90	27.69	0.00	103.81
CAB3–12–2	9.58	11.36	18.58	5.01	0.25	27.20	0.09	6.53	0.00	0.00	22.63	0.19	101.40
CAB3–16–3	2.93	13.05	10.52	3.29	0.00	34.35	0.00	9.95	0.00	0.00	26.47	0.00	100.56
CAB2q–14–4–1	5.96	8.59	15.65	5.05	0.00	35.83	0.00	4.81	0.02	0.00	21.37	0.63	97.91
CAB2q–14–4–2	4.89	8.30	17.97	5.45	0.00	38.95	0.00	4.38	0.00	0.00	21.57	0.81	102.32
CR1367–1b–2	10.22	10.95	13.92	5.28	0.28	20.48	0.32	12.80	1.11	0.56	23.92	0.01	99.85
Unknown # 2													
PR1372–1–1–1	3.57	1.50	0.06	10.03	0.54	4.92	1.40	54.01	0.00	7.63	17.62	0.03	101.31
PR1372–1–1–2	3.50	1.67	0.07	11.58	0.49	6.18	1.11	51.07	0.00	6.23	17.12	0.15	99.17
PR1372–1–4	4.69	1.41	0.03	16.95	1.07	6.63	4.75	44.45	0.00	3.36	17.70	0.00	101.04
Unknown # 3													
CAB10–8	8.35	9.64	11.23	7.30	0.01	4.33	0.00	8.14	25.37	0.16	25.88	0.00	100.41
Corrected weight percent (data corrected for the chromite and pentlandite (*) matrix effect)													
Unknown # 1													
CAB1–1		9.01	18.30	5.54	0.21	21.22	0.49	13.17	1.72	0.90	27.69	0.00	98.25
CAB3–12–2		6.87	18.58	5.01	0.25	27.20	0.09	6.53	0.00	0.00	22.63	0.19	87.35
CAB3–16–3		11.60	10.52	3.29	0.00	34.35	0.00	9.95	0.00	0.00	26.47	0.00	96.18
CAB2q–14–4–1		5.92	15.65	5.05	0.00	35.83	0.00	4.81	0.02	0.00	21.37	0.63	89.28
CAB2q–14–4–2		6.11	17.97	5.45	0.00	38.95	0.00	4.38	0.00	0.00	21.57	0.81	95.24
CR1367–1b–2		5.86	13.92	5.28	0.28	20.48	0.32	12.80	1.11	0.56	23.92	0.01	84.54
Unknown # 2													
PR1372–1–1–1		0.00	0.06	10.03	0.54	4.92	1.40	54.01	0.00	7.63	17.62	0.03	96.23
PR1372–1–1–2		0.00	0.07	11.58	0.49	6.18	1.11	51.07	0.00	6.23	17.12	0.15	94.02
PR1372–1–4		0.00	0.03	16.95	1.07	6.63	4.75	44.45	0.00	3.36	17.70	0.00	94.94
Unknown # 3													
CAB10–8 *		0.01	0.00	7.30	0.01	4.33	0.00	8.14	25.37	0.16	17.70	0.00	63.02
Atomic percent (calculated from corrected data)													
Unknown # 1													
CAB1–1		9.567	18.495	5.169	0.064	6.548	0.288	7.593	0.525	0.503	51.248	0.000	
CAB3–12–2		8.578	22.077	5.498	0.092	9.868	0.062	4.425	0.000	0.000	49.224	0.177	
CAB3–16–3		13.488	11.645	3.367	0.000	11.604	0.000	6.280	0.000	0.000	53.616	0.000	
CAB2q–14–4–1		7.793	19.603	5.840	0.000	13.700	0.000	3.436	0.006	0.000	49.001	0.622	
CAB2q–14–4–2		7.651	21.411	5.992	0.000	14.171	0.000	2.974	0.000	0.000	47.045	0.756	
CR1367–1b–2		7.400	16.731	5.860	0.102	7.513	0.222	8.771	0.401	0.371	52.619	0.011	
Unknown # 2													
PR1372–1–1–1		0.000	0.072	11.711	0.213	1.898	1.025	38.949	0.000	5.324	40.780	0.028	
PR1372–1–1–2		0.000	0.091	13.803	0.194	2.437	0.835	37.594	0.000	4.437	40.453	0.156	
PR1372–1–4		0.000	0.035	19.475	0.410	2.518	3.431	31.536	0.000	2.308	40.288	0.000	
Unknown # 3													
CAB10–8		0.010	0.000	12.770	0.010	2.500	0.000	8.790	14.440	0.170	61.310	0.000	

Samples: CAB1–1 refers to $(Ni,Fe,Cu)_2(Ir,Rh)S_3$ in Figure 4A, CAB2–14–4–1 and 14–4–2 to $(Ni,Fe,Cu)_2(Ir,Rh)S_3$ in Figure 4C, and CR1367–1b–2 to (Fe,Ni,Cu,Ir,Rh)S in Figure 3B. Prefixes: CR: Rio Creves, PR: Torrente Provola (Finero), CAB: Arroyo de los Caballos (Ojén).

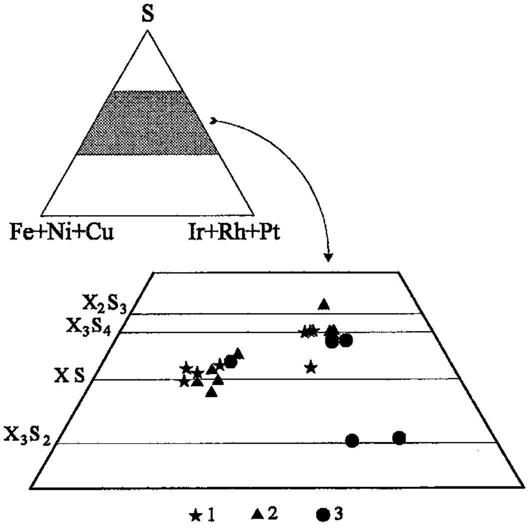

FIG. 2. Stoichiometry of the PGM investigated plotted in terms of S – (Fe+Ni+Cu) – (Ir+Rh+Pt). Minor amounts of Pd, Ru, and Os, where present, have been added to Ir+Rh+Pt. X_2S_3 to X_3S_2 horizontal lines represent ideal stoichiometries in terms of metal–sulfur proportions. Symbols: 1: compositions from Finero (Ferrario & Garuti 1990, Table 3), 2: compositions from Ojén (this work), 3: compositions from Finero (this work). Compositions referring to the same grain of cuprorhodsite, cuproiridsite, (Table 1) and unknown #2 (Table 2) have been averaged and plotted as single points.

the average formula being $(Cu_{0.80}Fe_{0.06}Ni_{0.03})_{\Sigma 0.89}$ $(Ir_{1.56}Rh_{0.51}Pd_{0.03}Ru_{0.03})_{\Sigma 2.13}S_{3.98}$. The compositions compare well with those reported by Ferrario & Garuti (1990) for optically similar phases (anal. 1 and 2, Table 3), although they were not recognized as cuproiridsite by those authors. They also described a yellowish, anisotropic Ir–Cu–Rh sulfide (Table 3, anal. 3, in Ferrario & Garuti 1990) containing appreciable Pt (3.53 at.%) and Ag (1.24 at.%). In spite of the differences in optical properties, the stoichiometry fits that of cuproiridsite.

Two grains of malanite were analyzed in the Ojén chromitites (CAB1-2-2 and CAB3-15-2, Table 1). The mineral is found associated with pentlandite and silicate in one case (Fig. 5A), and with pentlandite, irarsite, and an unidentified Pd-sulfide in the other (Fig. 5C). Pentlandite occupies most of the inclusion volume, and malanite and the other associated minerals are confined to the borders, in contact with the including chromite. The Ojén malanite is isotropic, white-grey, and more reflective than the associated pentlandite. Because of the small grain-size, Ni and Fe had to be corrected for the fluorescence effect from pentlandite. Resulting compositions for the two grains

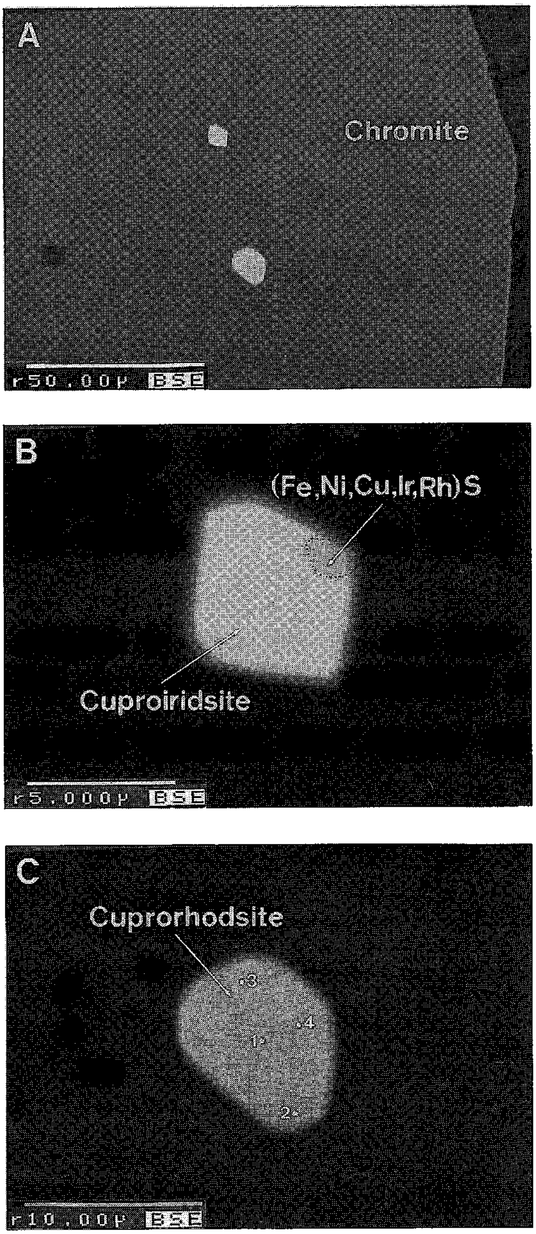

FIG. 3. A) Large-scale view of cuproiridsite (upper grain, CR1367–1b) and cuprorhodsite (lower grain, CR1367–1a) included in fresh chromite from Finero. B) Detail of A showing higher magnification of cuproiridsite (anal. CR1367–1b–1 and 1b–3, Table 1) intergrown with unknown #1, (Fe,Ni,Cu,Ir,Rh) sulfide (anal. CR1367–1b–2, Table 2). C) Detail of A showing higher magnification of cuprorhodsite and location of four points analyzed (Table 1, CR1367–1a–1 to 1a–4). The grain shows very small variations in composition. BSE images.

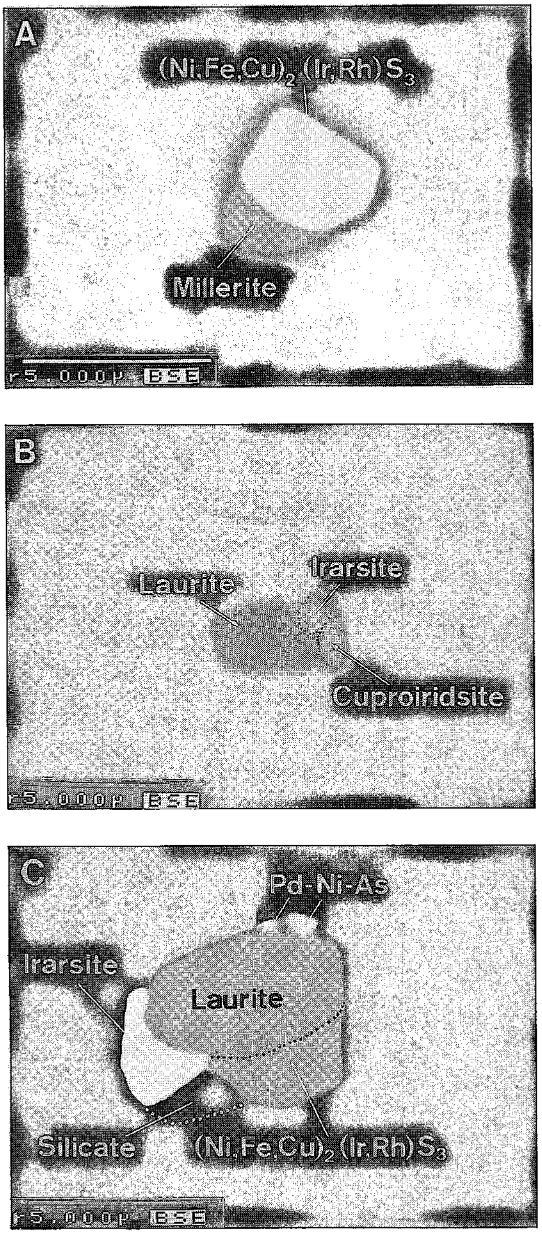

FIG. 4. A) Composite inclusion in chromite of Ojén consisting of unknown #1 and millerite. Unknown #1 roughly corresponds to (Ni,Fe,Cu)$_2$(Ir,Rh)S$_3$ (anal. CAB1–1, Table 2). B) Composite inclusion in chromite from Finero made up of laurite, irarsite, and cuproiridsite (anal. PO1355–4–2 and 4–4, Table 1). C) Composite inclusion in chromite from Ojén comprising laurite, irarsite, unidentified Pd–Ni–As, silicate, and unknown #1, roughly (Ni,Fe,Cu)$_2$(Ir,Rh)S$_3$ (anal. CAB2q–14a and 14b, Table 2). BSE images.

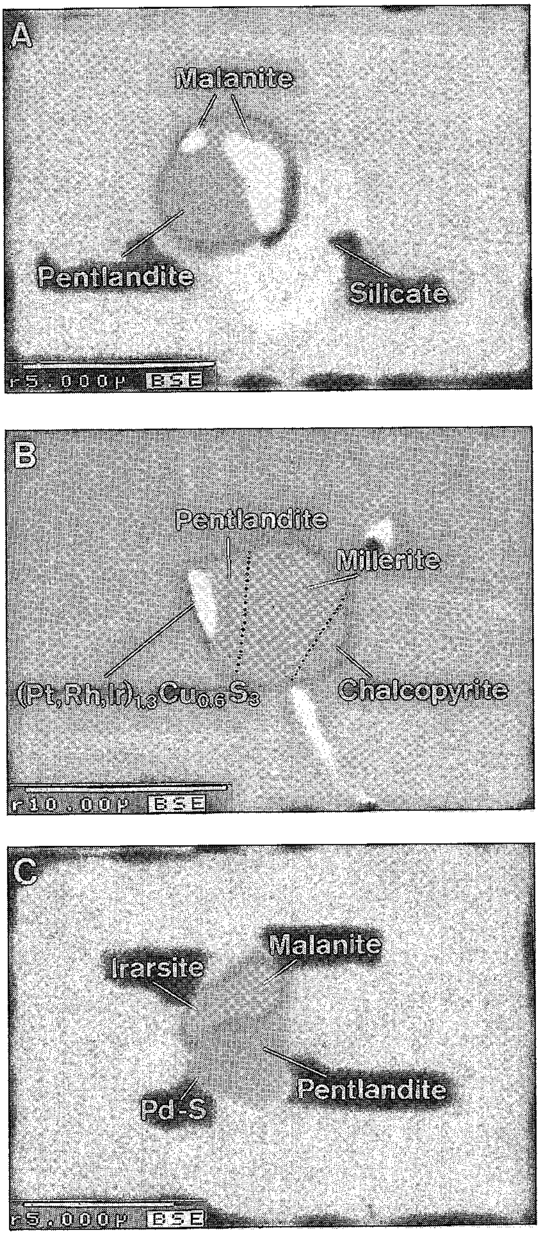

FIG. 5. A) Composite inclusion of malanite, pentlandite and silicate from the Ojén chromitite. Malanite refers to analysis CAB1–2–2 (Table 1). B) Composite inclusion in the Ojén chromite consisting of pentlandite, millerite, chalcopyrite, and unknown #3, possibly (Pt,Rh,Ir)$_{1.3}$Cu$_{0.6}$S$_3$, as deduced from analysis CAB10–8 (Table 2). C) Malanite (anal. CAB3–15–2, Table 1) associated with pentlandite, irarsite, and unidentified Pd–S. Polyphase inclusion in chromite from Ojén. BSE images.

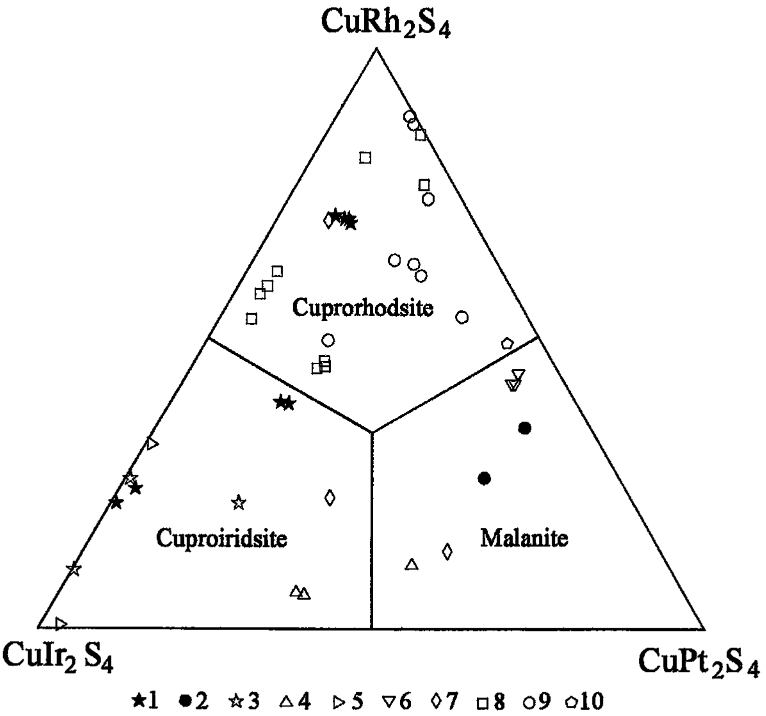

FIG. 6. Rh–Ir–Pt plot (in at. %) of compositions of cuprorhodsite, cuproiridsite, and malanite from Finero and Ojén chromitite, compared with data from the literature. Minor Pd, and (Ru+Os), where present, have been added to Pt and Ir, respectively. Symbols: 1: Finero (this work), 2: Ojén (this work), 3: Finero (Ferrario & Garuti 1990), 4: Upper Chindwin placers, northern Burma (Hagen *et al.* 1990), 5: Tiébaghi chromitites, New Caledonia (Augé 1988), 6: Joubdo placers, Ethiopia (Cabri *et al.* 1981), 7: Thetford Mines chromitites, Québec (Corrivaux & Laflamme 1990), 8: Durance placers, France (Johan *et al.* 1990), 9: Kamchatka placers, Russia (Rudashevsky *et al.* 1985), 10: Manampotsy placers, eastern Madagascar (Legendre & Augé 1992).

gave $(Cu_{0.92}Ni_{0.03})_{\Sigma0.95}(Pt_{1.02}Rh_{0.52}Ir_{0.41}Pd_{0.08})_{\Sigma2.03}S_{4.01}$ and $(Cu_{0.93}Fe_{0.06})_{\Sigma0.99}(Pt_{1.02}Rh_{0.69}Ir_{0.19}Pd_{0.10}Ru_{0.01})_{\Sigma2.01}S_4$, thus confirming the stoichiometry X_3S_4 (Peng *et al.* 1978, Fleischer *et al.* 1980, Cabri 1981) as opposed to XS_2 (Yu *et al.* 1974, Fleischer *et al.* 1976).

Cuprorhodsite, cuproiridsite, and malanite from Finero and Ojén are compared with other examples from the literature in the diagram $CuRh_2S_4$–$CuIr_2S_4$–$CuPt_2S_4$ (Fig. 6). The Finero cuprorhodsite is compositionally similar to cuprorhodsite from Thetford Mines (Corrivaux & Laflamme 1990) that also was found included in chromite, but differs slightly from cuprorhodsite from alluvial deposits of the Durance River, France (Johan *et al.* 1990), Kamchatka, Russia (Rudashevsky *et al.* 1985), and Manampotsy, eastern Madagascar (Legendre & Augé 1992) in their Ir and Pt contents. Four compositions of cuproiridsite from Finero plot along the $CuRh_2S_4$–$CuIr_2S_4$ join, being as Pt-poor as cuproiridsite from the Tiébaghi chromitites, New Caledonia (Legendre & Augé 1986). The other three examples of cuproiridsite from Finero are enriched in Pt, although not reaching the Pt contents of cuproiridsite from chromitite at Thetford Mines (Corrivaux & Laflamme 1990) and from placers in Burma (Hagen *et al.* 1990). The malanite from Ojén has Pt contents similar to that from placers in Ethiopia (Cabri *et al.* 1981) and Burma (Hagen *et al.* 1990), and from chromitite at Thetford Mines (Corrivaux & Laflamme 1990, unknown #2), but displays intermediate compositions with regard to the Ir–Rh reciprocal substitution. The data support the existence of wide ranges of solid solution among cuprorhodsite, cuproiridsite, and malanite, all pertaining to the space group *Fd*3*m* (cubic system). In particular, almost continuous solid-solution seems to occur parallel to the $CuRh_2S_4$–$CuIr_2S_4$ join, at variable mol fractions of malanite. Solid solution along the joins $CuRh_2S_4$–$CuPt_2S_4$ and $CuIr_2S_4$–$CuPt_2S_4$ appears

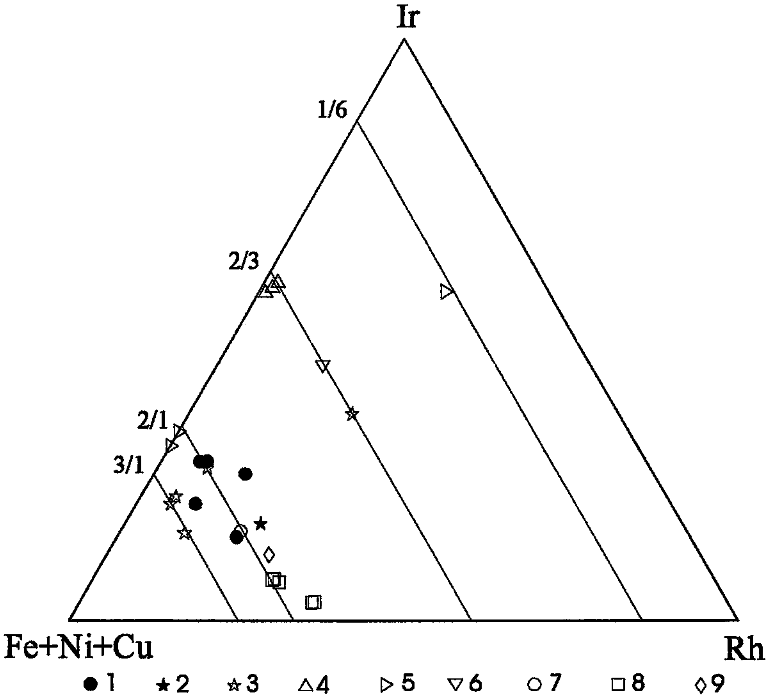

FIG. 7. Ir – Rh – (Fe+Ni+Cu) plot of composition (at. %) of (Ir,Rh)-rich Ni–Fe–Cu sulfides (unknown #1) and xingzhongite from Finero and Ojén chromitites compared with data from the literature. Minor (Pd+Pt), and (Ru+Os), where present, have been added to Rh and Ir, respectively. Symbols: 1: Ojén (this work), 2: Finero (this work), 3: Finero (Ferrario & Garuti 1990), 4: Tiébaghi chromitite, New Caledonia (Augé 1988), 5: unknown locality, China (Fleischer *et al.* 1976), 6: unknown locality, China (in Cabri & Laflamme 1981), 7: Thetford Mines chromitite, Québec (Corrivaux & Laflamme 1990), 8: Joubdo placers, Ethiopia (Cabri *et al.* 1981), 9: Tulameen placers, British Columbia (in Cabri & Laflamme 1981).

incomplete. In fact, the Pt-rich side of the triangular diagram is unoccupied, as all examples of malanite so far encountered in nature contain substantial Ir and Rh.

(Ir,Rh,Ni,Fe,Cu)S, probably xingzhongite

Among the PGM characterized by the monosulfide stoichiometry *XS*, one grain analyzed by Ferrario & Garuti (1990) from Finero (their Table 3, anal. 4) gave $(Ir_{0.34}Rh_{0.23}Cu_{0.18}Ni_{0.10}Fe_{0.11})_{\Sigma 0.96}S_{1.03}$, and was tentatively ascribed to xingzhongite, *i.e.*, (Ir,Cu,Rh)S, as provisionally defined by Cabri & Laflamme (1981). The mineral from Finero is described as a polygonal, single-phase grain (3 × 6.5 μm) included in chromite, typically bluish grey with weak anisotropism, and reflectance similar to laurite. Anisotropy, although weak, would be in contrast with the cubic structure proposed for xingzhongite (Fleischer *et al.* 1980). In this work, we have plotted the composition of the Finero xingzhongite in the diagram Ir – Rh – (Fe+Ni+Cu) (Fig. 7) and compared it with compositions from Tiébaghi, New Caledonia (Legendre & Augé 1986), and from China (Cabri & Laflamme 1981), although substantial Pb was found to be present in this latter case. We are aware that a proper definition of xingzhongite is still needed (Jambor 1989). Nevertheless, it is interesting to note that all compositions give a similar BM:PGE ratio of 2:3, and have Ir and Cu as the dominant PGE and BM, respectively, suggesting that xinzhongite possibly corresponds ideally to $Ir_3Cu_2S_5$. If correct, this inference would imply the existence of some structural control on the stoichiometry of xingzhongite. The composition of (Ir,Rh,Ni)S from China (Fleischer *et al.* 1976), also plotted, gives a BM:PGE of 1:6. The mineral, however, contains no Cu, is strongly anisotropic, in contrast with xingzhongite, and would appear to be a different species.

Unknown #1, probably $(Ni,Fe,Cu)_2(Ir,Rh)S_3$

Several grains of a monosulfide mineral corresponding to (Ni,Fe,Cu,Ir,Rh)S with (Ni+Fe+Cu) > (Ir+Rh) have been observed at Finero and Ojén. They are not PGM *sensu stricto*, but should more correctly be classified as PGE-rich base-metal sulfides. At both localities, the minerals occur as part of composite inclusions in chromite. Associations with cuproiridsite (Fig. 3B), with millerite (Fig. 4A), and with laurite, irarsite, unidentified Pd–Ni–As, and silicate (Fig. 4C) have been observed. But composite grains with laurite + cuproiridsite, laurite + pentlandite, and millerite + pentlandite also have been reported by Ferrario & Garuti (1990) at Finero. The minerals are grey to bluish grey, generally less reflective than millerite and pentlandite, and distinctly anisotropic. The six compositions obtained in this work (Table 2) and four from Ferrario & Garuti (1990) (Table 3, anal. 5 to 8) have been plotted in the diagram Ir – Rh – (Fe+Ni+Cu) (Fig. 7), and compared with similar monosulfides from an unknown locality in China (Fleischer *et al.* 1976), from placers in Ethiopia (Cabri *et al.* 1981) and at Tulameen, British Columbia (in Cabri & Laflamme 1981), and from chromitite at Thetford Mines (Corrivaux & Laflamme 1990). The (Ni+Fe+Cu)–(Ir+Rh) ratio varies from 1.6 to 3.1. Of the nineteen compositions plotted, three from Finero have a ratio of 3, and eleven, including six from various occurrences, are in the range 1.73–2.14, averaging 1.96. The stoichiometry $(Ni,Fe,Cu)_2(Ir,Rh)S_3$ would appear the most likely, with the Ir-for-Rh substitution covering the entire range. It is still an open question whether these (Ir,Rh)-rich Ni–Fe–Cu sulfides are new mineral species or represent PGE-rich pyrrhotite and pentlandite, as discussed by Cabri & Laflamme (1981). Attribution to the pentlandite species would be possible only for CAB3–12–2 and CAB2q–14a and b (Table 2), which show high Ni/Fe values (close to 3) and pentlandite-type sulfur-deficiency, although the anisotropism of the minerals contradicts this conclusion. The possibility of PGE-rich pyrrhotite is supported by the consideration that the (Ir,Rh)-rich nature of the minerals might reflect the preferential solubility of these PGE in pyrrhotite (Cabri & Laflamme 1981), as deduced from experimental data. However, the observation made in this work that the substitution of PGE for base metals occurs according to fixed proportions, if confirmed, could be consistent with the existence of a new mineral.

Unknown #2, probably $(Rh,Cu)_3S_2$

Two grains have the metal-excess stoichiometry X_3S_2, with compositions corresponding to the formulas $(Rh_{1.92}Pd_{0.24}Ir_{0.11}Ru_{0.05}Cu_{0.64})_{\Sigma 2.96}S_{2.04}$ and $(Rh_{1.58}Pd_{0.11}Ir_{0.12}Ru_{0.17}Cu_{0.97})_{\Sigma 2.95}S_{2.12}$ (samples PR1372–1–1 average, and PR1372–1–4, Table 2). The grains were found at Finero, intergrown with minor Cu-sulfide, possibly digenite, forming a single inclusion in chromite. External morphology of the inclusion is polygonal, although individual PGM are apparently anhedral and occupy most of the inclusion volume. Both grains are white-grey, probably isotropic, and definitely more reflective than the associated sulfide. The mineral may correspond to prassoite, the stoichiometry of which is not known exactly, but provisionally described as $Rh_{17}S_{15}$ by Cabri & Laflamme (1981), or Rh_3S_4 by Augé (1988). The present compositions display an anomalous metal-excess with respect to those from the literature, but the predominance of Rh and Cu in the mineral composition is possibly consistent with prassoite.

Unknown #3, Pt,Rh,Ir,Cu sulfide

This mineral was found in one composite inclusion at Ojén, associated with pentlandite, millerite and chalcopyrite (Fig. 5B). It appears optically similar, but not identical, to malanite, being white-grey with a faint bluish tint, probably isotropic, and more reflective than the associated (Ni,Fe,Cu)-sulfides. After correction for fluorescence effects due to chromite and pentlandite, its composition displays an excess in sulfur compared to malanite (CAB10–8, Table 2), and can be recalculated to the formula $(Pt_{0.72}Rh_{0.43}Ir_{0.12}Pd_{0.01})_{\Sigma 1.28}Cu_{0.64}S_{3.06}$, which would correspond to the X_2S_3 stoichiometry of kashinite, $(Ir,Rh)_2S_3$ (Begizov *et al.* 1975, 1985) or bowieite, $(Rh,Ir)_2S_3$ (Desborough & Criddle 1984), with Pt as the dominant PGE and a substantial amount of Cu. There is the possibility, however, that the mineral is (Ni,Fe)-rich malanite if part of the Ni and Fe, previously subtracted for the pentlandite correction, is left to balance the sulfur excess. The present data are not conclusive, owing to analytical uncertainties caused by the small grain-size; therefore, the true composition of the unknown #3 remains undetermined.

CONCLUDING REMARKS

The systematic electron-microprobe investigation of Ir-, Rh-, and Pt-bearing sulfides in chromitites of Finero and Ojén allows the following inferences to be drawn:

1) Cuprorhodsite, cuproiridsite, and malanite from Finero and Ojén cover a wide range of composition in the system $CuRh_2S_4$–$CuIr_2S_4$–$CuPt_2S_4$; combined with data from the literature, they confirm the existence of extensive solid-solution among the three end-members, although Pt-rich phases close to pure malanite have not yet been found in nature.

2) The (Ir,Rh)-rich, Ni–Fe–Cu sulfides discovered at Finero and Ojén, together with similar sulfides from the literature, have a quite constant stoichiometry,

close to $(Ni,Fe,Cu)_2(Ir,Rh)S_3$. Further investigation is needed to prove whether the group represents an independent mineral species or corresponds to PGE-rich pyrrhotite and pentlandite.

3) Other minerals analyzed may correspond to xingzhongite $(Ir,Rh)_3(Ni,Fe,Cu)_2S_5$, to unknown $(Rh,Cu)_3S_2$, and to an unidentified Pt,Rh,Ir,Cu sulfide, possibly $(Pt,Rh,Ir)_{1.3}Cu_{0.6}S_3$ or (Ni,Fe)-rich malanite.

4) It is interesting to note that cuprorhodsite, cuproiridsite, malanite, and the (Ir,Rh)-rich Ni–Fe–Cu sulfides are well known from placers deposits; they are found associated with nuggets, commonly included in or intergrown with Pt–Fe alloys. In many cases, the placers bear a genetic relation with Alaskan-type complexes (Cabri *et al.* 1981, Cabri & Laflamme 1981, Rudashevsky *et al.* 1985), although in others, the Alaskan-type origin has been tentatively inferred, partly on the basis of the presence of these PGM (Johan *et al.* 1990, Legendre & Augé 1992). A possible derivation from ophiolites, however, has been proposed for placers containing the Pt–Fe alloys with associated Ir–Rh–Pt sulfides, in Burma (Hagen *et al.* 1990). That ophiolites could be the primary source of these Ir–Rh–Pt sulfides is supported by the finding of the PGM *in situ*, within podiform chromitite, for example at Tiébaghi, New Caledonia (Legendre & Augé 1986, Augé 1988), and Thetford Mines, Québec, where a primary relation of the Ir–Rh–Pt sulfides with isoferroplatinum has even been documented (Corrivaux & Laflamme 1990). The present investigation indicates that an assemblage of primary PGM, relatively enriched in Ir–Rh–Pt sulfides, can also be associated with podiform chromitite from orogenic lherzolite massifs emplaced into granulitic belts, such as those of Finero and Ojén. This type of ultramafic complex could be a possible source for the Ir–Rh–Pt sulfide mineralization in placer deposits, although a primary association of the sulfides with Pt–Fe alloys has not been observed. In conclusion, the use of these minerals as markers of an Alaskan-type origin of the placers should be considered with caution, where a spatial relation with the source rocks cannot be demonstrated (Legendre & Augé 1992).

5) Most of the PGM recognized at Finero and Ojén represent the first finding of these minerals in Italy and Spain.

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