

## GENETIC RELATIONSHIPS BETWEEN BASE-METAL SULFIDES AND PLATINUM-GROUP MINERALS IN THE YANGLIUPING Ni-Cu-(PGE) SULFIDE DEPOSIT, SOUTHWESTERN CHINA

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### ABSTRACT

The Yangliuping Ni-Cu-(PGE) sulfide deposit in southwestern China is hosted by a series of mafic-ultramafic sills that intrude Devonian strata. Massive sulfides and disseminated sulfides occur at the base of the sills. Minor massive sulfide veins occur in footwall fractures. The major base-metal sulfides (BMS) are pyrrhotite, pentlandite, and chalcopyrite. The most common PGE-bearing sulfarsenide is a Pd-bearing cobaltite-gersdorffite solid solution. Other PGM identified include sperrylite, testibiopalladite, and Pd-bearing melonite. All grains of the cobaltite-gersdorffite solid solution and PGM are enclosed in pyrrhotite and pentlandite. Both the PGM and their host BMS have been partially altered in place by hydrothermal fluids. Electron-microprobe analyses show that pyrrhotite and pentlandite contain up to 0.1–0.5 wt% Pt. Euhedral grains of cobaltite-gersdorffite solid solution (<30  $\mu\text{m}$  in diameter) are zoned, with a Rh-Pt-Ni-rich core containing up to 6.4 wt% Rh and 0.5% Pt, and a Co-rich margin. Textural relations suggest that the Pt-bearing cobaltite-gersdorffite solid solution crystallized before exsolution of pentlandite from monosulfide solid-solution *i.e.*, probably above >600°C based on the phase relations of the system FeAsS-NiAsS-CoAsS. Sperrylite and testibiopalladite crystals are up to 50–80  $\mu\text{m}$  in diameter and are compositionally homogeneous. Some testibiopalladite crystals occur in the contact of two pyrrhotite grains. Monosulfide solid-solution was the first phase to crystallize from a sulfide melt, and it then exsolved to pyrrhotite and pentlandite. Pt and Pd became enriched in the residual sulfide liquid, and crystallized as PGM and Pd-bearing cobaltite-gersdorffite solid solution at a lower temperature. Minor Pt and Pd in *Mss* were finally expelled from the structure below 800°C.

*Keywords:* platinum-group minerals, base-metal sulfides, fractional crystallization, sulfide melt, Yangliuping, China.

### SOMMAIRE

Des filons-couches mafiques et ultramafiques qui recoupent une séquence sédimentaire dévonienne sont l'hôte du gisement de sulfures à Ni, Cu et éléments du groupe du platine de Yangliuping, dans le sud-ouest de la Chine. Les sulfures massifs ou disséminés sont situés à la base des filons-couches. Des sulfures massifs occupent aussi des veines en petits volumes dans le socle. Les minéraux de métaux de base les plus importants sont pyrrhotite, pentlandite, et chalcopyrite. Le sulfarsénite le plus courant est une solution solide cobaltite-gersdorffite contenant du palladium. Les minéraux du groupe du platine suivants ont aussi été identifiés: sperrylite, testibiopalladite, et melonite palladifère. Tous les grains de solution solide cobaltite-gersdorffite et les minéraux du groupe du platine sont inclus dans la pyrrhotite et la pentlandite. Ces minéraux ont partiellement été altérés par une phase fluide. Les analyses à la microsonde électronique montrent que la pyrrhotite et la pentlandite contiennent jusqu'à 0.1–0.5% Pt (en poids). Les grains idiomorphes de solution solide cobaltite-gersdorffite (<30  $\mu\text{m}$  de diamètre) sont zonés, avec un coeur riche en Rh, Pt et Ni, contenant jusqu'à 6.4% Rh et 0.5% Pt, et une bordure riche en Co. Les relations texturales font penser que la solution solide cobaltite-gersdorffite platinifère a cristallisé avant l'exsolution de la pentlandite de la solution solide monosulfurée, et donc à une température supérieure à 600°C, selon les relations de phase dans le système FeAsS-NiAsS-CoAsS. Les cristaux de sperrylite et de testibiopalladite, entre 50 et 80  $\mu\text{m}$  de taille, sont homogènes. Certains cristaux de testibiopalladite se trouvent à l'interface entre grains de pyrrhotite. La solution solide monosulfurée était la première espèce à cristalliser aux dépens d'un liquide sulfuré, et celle-ci s'est par la suite décomposée en pyrrhotite et pentlandite. Le platine et le palladium sont

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devenus enrichis dans le liquide sulfuré résiduel, et sont apparus sous forme de minéraux du groupe du platine inclus dans la solution solide cobaltite–gersdorffite à température plus faible. Le Pt et le Pd, logés dans la solution solide monosulfurée en quantités mineures, ont par la suite été libérés de la structure en refroidissant au delà de 800°C.

(Traduit par la Rédaction)

*Mots-clés:* minéraux du groupe du platine, sulfures des métaux de base, cristallisation fractionnée, liquide sulfuré, Yangliuping, Chine.

## INTRODUCTION

The Yangliuping Ni–Cu–(PGE) sulfide deposit is hosted by mafic-ultramafic sills of the Emeishan Large Igneous Province (ELIP). The ELIP covers an area of more than  $5 \times 10^5$  km<sup>2</sup> on the western margin of the Yangtze Block and the eastern margin of the Tibetan Plateau, southwestern China (Fig. 1). The emplacement of the magmas is dated at 260 Ma (Zhou *et al.* 2002a). The Yangliuping Ni–Cu–(PGE) sulfide deposit was discovered and explored in the 1970s by the Bureau of Geology and Mineral Resources of Sichuan Province (BGMS), and is the first deposit to be related to a large igneous province in China (Zhou *et al.* 2002b). The mafic-ultramafic sills are distributed within the Yangliuping tectonic dome (Song *et al.* 2003) (Fig. 1). Three types of ores, massive and disseminated sulfide and vein sulfide, are present at Yangliuping. The proven metal reserves of the deposit are ~100,000 tonnes of Ni, ~63,000 tonnes of Cu, and ~17 tonnes of platinum-group elements (PGE). The average grade is 0.45 wt% Ni, 0.16 wt% Cu, and 0.55 ppm total PGE (BGMS 1982). The sulfide orebodies occur near the bottom of the mafic-ultramafic sills and are hosted by serpentinite. The textural and geochemical characteristics indicate that the sulfide mineralization is magmatic in origin (Song *et al.* 2003).

More than 40 opaque minerals, including base-metal sulfides (BMS), sulfarsenides, Fe–Ti oxides, and platinum-group-minerals (PGM), were identified by Li *et al.* (2000), who described mineral assemblages in the three types of ores. They also reported results of a few electron-microprobe analyses of the principal PGM. However, the detailed textural relations between BMS and PGM have not been systematically studied. The disseminated ores have experienced intense late-stage alteration. In contrast, the massive ores preserve original assemblages of magmatic minerals (Song *et al.* 2003). In this study, we investigate the textural relations between the BMS and PGM, and provide analytical data for these minerals.

## GEOLOGICAL BACKGROUND

The Yangliuping area is a dome structure consisting of Devonian–Triassic strata (Fig. 1), which underwent greenschist-facies metamorphism in the Late Triassic (BGMS 1991, Arne *et al.* 1997). The Devonian strata

consist of quartzite, graphite-bearing schist, mica schist, and graphite-bearing marble. The Carboniferous strata are composed of calcareous slate and mica schist, with marble and quartzite intercalations. The Early Permian strata include marble with schist and slate intercalations; they conformably overlie the Carboniferous strata. The Late Permian Emeishan flood basalt sequence (500–1500 m thick; Song *et al.* 2001, Zhou *et al.* 2002a), comprises lavas, tuffs and agglomerates, which conformably overlie the Early Permian strata and are overlain conformably by Late Permian metasandstone.

Four mafic-ultramafic sills, Yangliuping, Zhengziyanwu, Xiezuoping, and Daqiangyanwu, were emplaced into the Devonian sequence of carbonaceous marble and schist. The sills have experienced intense late-magmatic hydrothermal alteration, and late Triassic greenschist-facies regional metamorphism. From the bottom to the top, the mineralized sills consist of serpentinite (40–60% by volume), talc schist (25–40%), tremolite schist (10–30%), and altered gabbro (5–7%). The Yangliuping sill is about 2000 m long, about 300 m thick and dips to the west and southwest. The mineralization is restricted to the lower parts of the sills, where disseminated sulfide grades downward into massive ore. In the disseminated sulfides, sulfide minerals are interstitial to cumulus olivine and pyroxene that are now replaced by serpentine. These relationships suggest that the orebodies were formed by segregation of an immiscible sulfide liquid, which settled to the lower part of the sills. The massive and disseminated sulfides have a low Pd:Ir ratio (4–39) (Song *et al.* 2003), consistent with a magmatic origin; hydrothermal deposits typically have a very high Pd:Ir ratio (Keays *et al.* 1982).

## SAMPLING AND ANALYTICAL METHODS

More than 100 polished thin sections were prepared from samples of the three different types of ore taken from exploration and mining tunnels. The base-metal sulfides and platinum-group minerals were identified using reflected light microscopy. Chemical compositions of minerals were determined by wavelength-dispersion X-ray emission spectrometry using a JEOL electron microprobe. The accelerating voltage was 15 kV, the beam current was 20 nA, and the counting time was 20 seconds. Pure metals (Pt, Pd, Rh, Te, Ni, and Co) and sulfides (BiS<sub>2</sub>, FeS<sub>2</sub>, CuFeS<sub>2</sub>, ZnSe, PbS, SbS<sub>3</sub>,

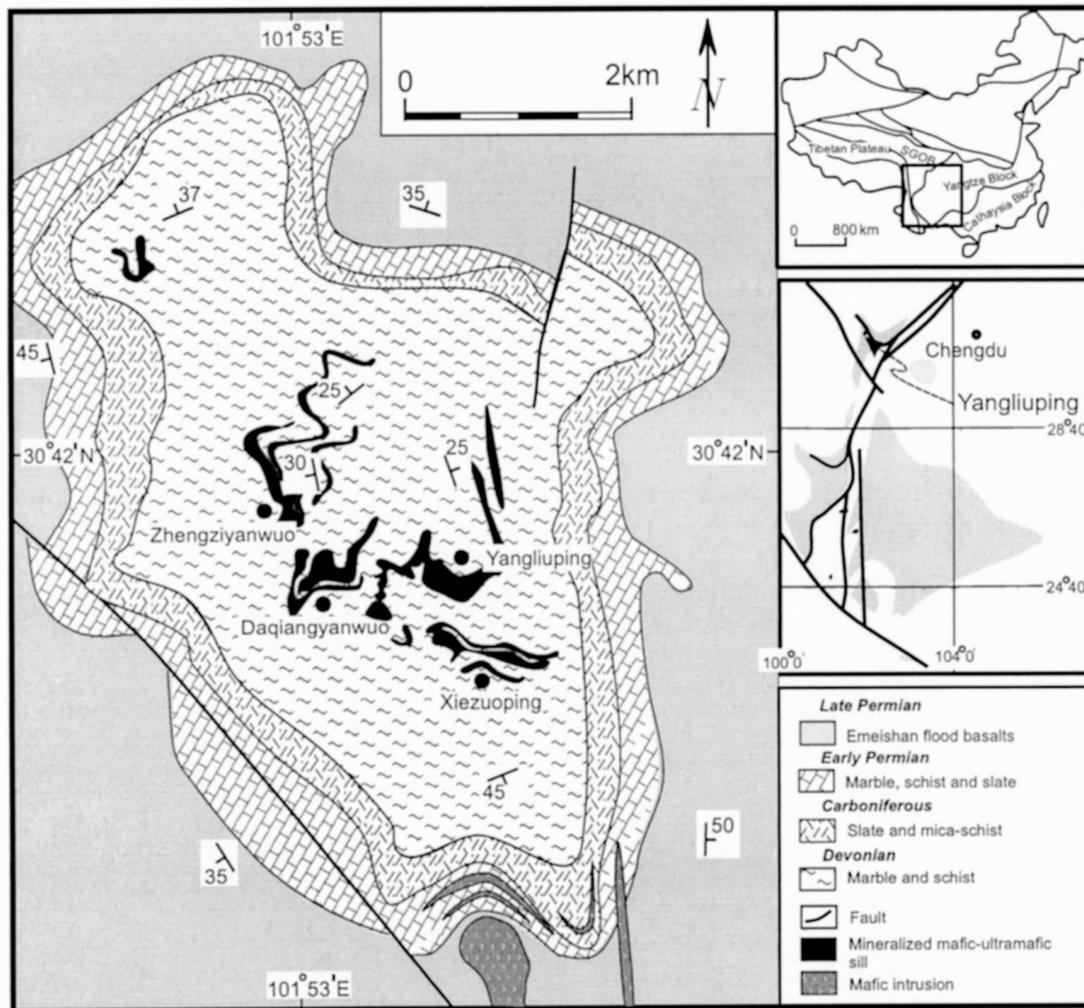


FIG. 1. Geological map of the Yangliuping tectonic dome, southwestern China, showing the distribution of mafic-ultramafic sills within the dome. Modified after Li *et al.* (2000) and Song *et al.* 2003).

and FeAsS) were obtained from the National Standard Committee of China and used as standards.

#### MINERALOGY

##### Base-metal sulfides

Pyrrhotite, pentlandite and chalcopyrite are the primary BMS in the massive ores. The proportions of pyrrhotite, pentlandite, and chalcopyrite are about 80:15:5. Massive ores also contain cobaltite–gersdorffite solid solution, violarite, and PGM, including sperrylite, testibiopalladite, sudburyite, omeiite, michenerite, Pd-

bearing melonite, and two unnamed PGM:  $(\text{Ni}, \text{Pd})_2(\text{Sb}, \text{Bi}, \text{Te})$  and  $\text{Pd}_2\text{Sb}$  (Li *et al.* 2000).

Pyrrhotite grains in the massive ores are up to 5 mm in diameter. Electron-microprobe analyses show that Ni contents of the pyrrhotite vary from 0.7 to 2.1 wt%, and Ni content decreases from the center to the margin of the crystals (Table 1). Analyses of some spots within pyrrhotite grains show concentrations of Pt as high as 0.5 wt% (Table 1).

As found in the experimental products of the crystallization of a sulfide melt (Kelly & Vaughan 1983), pentlandite occurs as a rim around pyrrhotite grains, as oriented lamellae and as blades along fractures within

TABLE 1. CHEMICAL COMPOSITION OF PYRRHOTITE AND PENTLANDITE IN THE SULFIDE ORES OF THE YANGLIUPING DEPOSIT, SOUTHWESTERN CHINA

Position	Fe	Co	Ni	Pt	S	Total	Fe	Co	Ni	Pt	$\Sigma$	S	
<b>Pyrrhotite in massive ores</b>													
Y01-39-17	M	59.2	0.1	0.8		38.4	98.5	7.07	0.01	0.09		7.17	8
Y01-39-16	C	58.8	0.1	1.1	0.5	38.8	99.3	6.96	0.01	0.12	0.02	7.11	8
Y01-40-4	M	59.8	0.1	1.0		38.1	99.0	7.21	0.01	0.12		7.34	8
Y01-40-5	C	59.2	0.1	1.8		38.0	99.1	7.16	0.01	0.21		7.38	8
Y01-47-13	C	61.9	0.1	1.0		36.9	99.8	7.71	0.01	0.12		7.84	8
Y01-57-3	C	59.7	0.1	1.1		38.5	99.4	7.11	0.01	0.12		7.25	8
Z01-42-2	M	59.5	0.1	1.5	0.1	39.6	100.8	6.89	0.01	0.16		7.07	8
Z01-42-3	C	57.9	0.2	2.1	0.5	39.9	100.5	6.67	0.02	0.23	0.02	6.93	8
<b>Pyrrhotite in disseminated ores</b>													
Z01-5-2	C	58.5	0.1	1.9		39.4	99.8	6.81	0.01	0.21		7.03	8
Z01-5-1	C	58.6	0.1	1.8	0.3	39.7	100.4	6.78	0.01	0.19	0.01	7.00	8
<b>Pentlandite in massive ores</b>													
Y01-40-3	F	33.7	0.7	33.6		31.4	99.3	4.94	0.09	4.68		9.71	8
Y01-47-12	F	30.7	0.7	35.6		31.9	99.1	4.42	0.10	4.88		9.40	8
Y01-57-4	F	31.8	0.8	35.2		32.0	99.7	4.58	0.10	4.81		9.49	8
Y01-47-5	F	31.3	0.9	34.9		34.1	101.2	4.21	0.12	4.47		8.80	8
Y01-40-2	R	30.8	1.1	36.0		32.0	100.0	4.41	0.15	4.91		9.48	8
Y01-45-7	R	30.6	1.3	35.6		31.9	99.4	4.41	0.18	4.88		9.46	8
Y01-39-18	R	30.6	1.4	36.3	0.2	33.5	101.9	4.20	0.18	4.73	0.01	9.12	8
Y01-56-2	R	31.2	1.4	34.8		31.8	99.2	4.51	0.20	4.79		9.50	8
Y01-39-15	R	29.7	1.5	36.1	0.2	33.6	101.1	4.07	0.19	4.69	0.01	8.97	8

Position of the sample: M: margin of the grain, C: center of the grain, R: rim of the grain, F: flame. Compositions are first quoted in weight %, then in atoms per formula unit.

pyrrhotite grains (Figs. 2A, B). Pentlandite contains 33.3 to 37.4 wt% Ni and less than 0.2% Pt. Rim pentlandite contains higher Co than lamellar pentlandite (1.1–2.5 versus 0.9%) (Table 1).

Chalcopyrite occurs as anhedral grains or as a polycrystalline intergrowth associated with pyrrhotite (Fig. 2C) and is more concentrated in the margins than in the center of a massive sulfide orebody. Except Cu and Fe, other elements, such as Ni, As, and Co, were not detected (Table 2).

There are only minor quantities of pyrite, violarite, sphalerite, galena, and linnaeite in the massive ores. Granular magnetite and ilmenite are the predominant oxides in these samples.

#### *Cobaltite–gersdorffite solid solution*

Cobaltite–gersdorffite, a solid-solution series between CoAsS and NiAsS, is commonly associated with arsenopyrite (FeAsS). Cobaltite–gersdorffite solid solution containing substantial levels of the PGE, such as found at Yangliuping, is rare elsewhere (Cabri & Laflamme 1976, Distler & Laputina 1979, Gervilla *et al.* 1997, Barkov *et al.* 1999).

The cobaltite–gersdorffite solid solution in the massive ores commonly occurs as single-crystal inclusions (10–30  $\mu\text{m}$  across) in pyrrhotite grains (Fig. 2D) and occasionally in pentlandite grains (Fig. 2E). The grains are idiomorphic, with a light ivory color, have a high

TABLE 2. CHEMICAL COMPOSITIONS OF CHALCOPYRITE FROM THE MASSIVE ORES OF THE YANGLIUPING DEPOSIT, SOUTHWESTERN CHINA

Sample	Fe	Cu	S	Total	Fe	Cu	$\Sigma$	S
Y01-42-1	30.9	34.2	34.9	100.0	0.48	0.50	0.98	1
Y01-41-6	31.1	32.7	34.9	98.8	0.48	0.47	0.96	1
Y01-41-5	31.1	33.9	35.0	100.0	0.48	0.49	0.97	1

Compositions are first quoted in weight %, then in atoms per formula unit.

reflectivity, are orthorhombic and weakly anisotropic, and form pseudocubic six-sided and occasionally four-sided cross-sections. Ni, Co and Fe contents of the cobaltite–gersdorffite solid solution vary from 9.8 to 15.8, 10.5 to 21.7, and 7.1 to 9.0 wt%, respectively. The cobaltite–gersdorffite solid solution contains from <0.1% to 6.4% Rh, less than 0.4% Pd, and less than 0.5% Pt (Table 3). Ni, Co, Rh, and Pt contents in the cobaltite–gersdorffite solid solution vary from grain to grain, some grains showing evidence of zoning. X-ray area scans of grains Y01-45-1, -2, and -3 (Fig. 3, Table 3) show a distinct compositional zoning, with a slightly Rh-enriched bean-shaped core, through a Ni-enriched mantle, to a Co-enriched margin. The PGE content of the core is much higher than that of either the margin of the zoned grains or the homogeneous grains. As shown in Figure 4A, the atomic proportion of (Pt + Pd + Rh) in

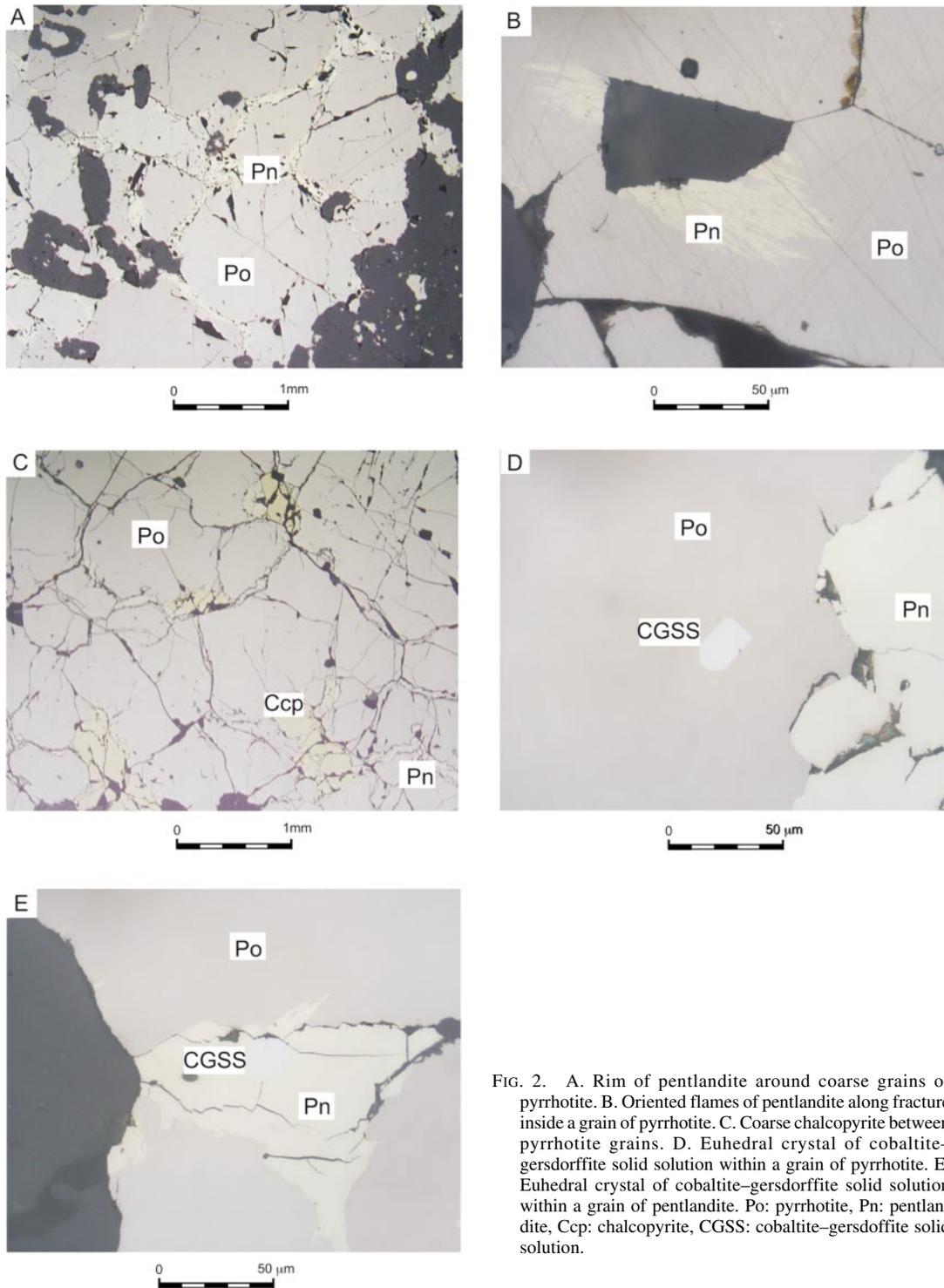


FIG. 2. A. Rim of pentlandite around coarse grains of pyrrhotite. B. Oriented flames of pentlandite along fracture inside a grain of pyrrhotite. C. Coarse chalcopyrite between pyrrhotite grains. D. Euhedral crystal of cobaltite-gersdorffite solid solution within a grain of pyrrhotite. E. Euhedral crystal of cobaltite-gersdorffite solid solution within a grain of pentlandite. Po: pyrrhotite, Pn: pentlandite, Ccp: chalcopyrite, CGSS: cobaltite-gersdorffite solid solution.

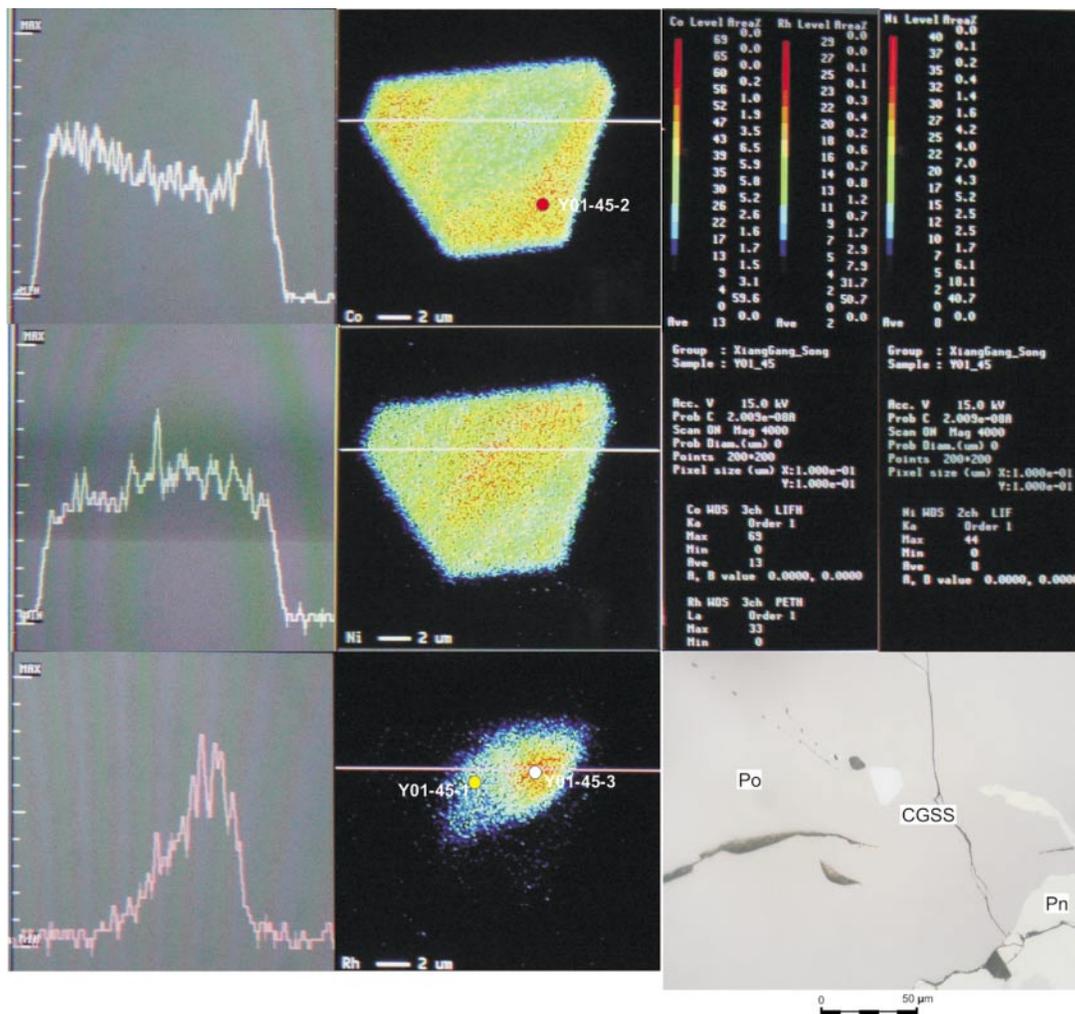


FIG. 3. X-ray area scans and compositional sections of Co, Ni, and Rh of a six-sided grain of cobaltite-gersdorffite solid solution embedded in pyrrhotite. It has a Rh-enriched core, a Ni-enriched mantle, and a Co-enriched margin. The compositions are shown in Table 3 (Y01-45-1, 2, and 3). The grain of the cobaltite-gersdorffite solid solution is shown in the middle of the photo in the lower-right corner. Po: pyrrhotite, Pn: pentlandite, CGSS: cobaltite-gersdorffite solid solution.

the core correlates negatively with Ni content, and correlates positively with S content (Table 3). In addition, the proportion of (Ni + Pt + Pd + Rh) correlates negatively with that of Co (Fig. 4B).

#### Platinum-group minerals

The three most common PGM in massive ores in the Yangliuping Ni-Cu-(PGE) deposit are sperrylite, testibiopalladite, and Pd-bearing melonite. Accessory PGM, including sudburyite, michenerite, omeiite, Pd-Sb-Bi telluride, Pd antimonide, and Os-Ir-Ru arsenide,

were identified using electron-microprobe data (Li *et al.* 2000). These PGM belong to three different groups: (1) Pd-Sb-Bi tellurides: testibiopalladite, michenerite, and two unnamed minerals; (2) Pt and Os arsenides: sperrylite, omeiite, and an unnamed mineral, and (3) Pd antimonides: sudburyite and two unnamed minerals.

Sperrylite forms subhedral grains up to  $80 \times 50 \mu\text{m}$  embedded in pyrrhotite. It is bright silver-gray. Figures 5A and B show that sperrylite grains and their host BMS appear to have been partially dissolved by late hydrothermal fluids along the contact with silicates. Sperrylite contains 52.3–55.7 wt% Pt, 40.7–44.6% As, 1.1–2.1%

TABLE 3. CHEMICAL COMPOSITION OF Pd-BEARING COBALTITE-GERSDORFFITE SOLID SOLUTION FROM THE MASSIVE ORES OF THE YANGLIUPING DEPOSIT, SOUTHWESTERN CHINA

Sample	Position	Fe	Co	Ni	Rh	Pt	Pd	Se	S	As	Total
Y01-39-9		8.4	18.6	10.5	0.4	0.1	0.2	0.1	18.9	44.0	101.3
Y01-40-1		8.1	19.4	9.2			0.1	0.2	19.6	43.9	100.6
Y01-45-1	C	7.8	14.5	13.3	1.7	0.1	0.3	0.1	18.3	45.0	101.1
Y01-45-2	M	7.1	21.7	9.2	0.2	0.1	0.1	0.1	19.1	45.4	103.1
Y01-45-3	C	7.2	12.8	12.2	4.5	0.3	0.3	0.1	17.8	43.9	99.2
Y01-45-6	M	7.1	18.2	12.2	0.0	0.2	0.2	0.1	18.7	45.4	102.1
Y01-47-1		7.9	12.2	15.9				0.0	18.9	45.4	100.5
Y01-47-11		8.7	13.2	13.4			0.3	0.2	19.2	43.8	98.8
Y01-47-14	C	7.5	11.5	14.3	3.1	0.4	0.2	0.2	17.2	44.4	98.8
Y01-47-15	C	7.3	10.5	15.8	2.0	0.5	0.2	0.1	17.1	45.2	98.7
Y01-47-16	M	7.9	17.6	11.6			0.3	0.2	18.8	45.0	101.7
Y01-47-17	M	7.9	15.2	14.1	0.1	0.3	0.2	0.1	19.0	45.1	101.9
Y01-47-2		9.0	13.3	13.7				0.2	19.8	44.4	100.5
Y01-47-3		8.3	11.9	15.3				0.1	19.4	45.0	100.1
Y01-47-7		7.3	12.7	15.4			0.2	0.2	17.4	46.0	99.2
Y01-52-1	C	8.0	15.5	11.8	2.2		0.4	0.2	18.5	44.5	101.0
Y01-52-2	C	8.8	12.5	9.8	6.4	0.1	0.4	0.1	19.0	42.1	99.5
Y01-57-1		7.6	15.2	10.0			0.2	0.2	19.4	46.6	99.4

Sample	Fe	Co	Ni	Rh	Pt	Pd	Σ	Se	S	As	Σ
Y01-39-9	0.254	0.536	0.304	0.007	0.001	0.003	1.105	0.002	1.001	0.997	2.0
Y01-40-1	0.242	0.548	0.260			0.002	1.051	0.003	1.020	0.977	2.0
Y01-45-1	0.238	0.419	0.385	0.028	0.001	0.004	1.074	0.002	0.974	1.024	2.0
Y01-45-2	0.210	0.613	0.259	0.003	0.001	0.002	1.087	0.002	0.990	1.008	2.0
Y01-45-3	0.225	0.379	0.365	0.077	0.003	0.005	1.053	0.002	0.971	1.027	2.0
Y01-45-6	0.213	0.519	0.350	0.000	0.002	0.003	1.086	0.002	0.979	1.019	2.0
Y01-47-1	0.236	0.347	0.453			0.000	1.037	0.001	0.986	1.014	2.0
Y01-47-11	0.262	0.377	0.383			0.004	1.026	0.003	1.010	0.986	2.0
Y01-47-14	0.236	0.343	0.429	0.054	0.004	0.004	1.069	0.005	0.949	1.046	2.0
Y01-47-15	0.228	0.312	0.473	0.034	0.005	0.002	1.054	0.003	0.938	1.058	2.0
Y01-47-16	0.236	0.502	0.332		0.002	0.003	1.076	0.003	0.986	1.010	2.0
Y01-47-17	0.235	0.432	0.400	0.001	0.002	0.003	1.074	0.002	0.990	1.008	2.0
Y01-47-2	0.265	0.371	0.386				1.022	0.003	1.018	0.979	2.0
Y01-47-3	0.246	0.334	0.432				1.013	0.002	1.003	0.995	2.0
Y01-47-7	0.225	0.370	0.452			0.002	1.050	0.004	0.938	1.058	2.0
Y01-52-1	0.244	0.448	0.343	0.036		0.006	1.076	0.003	0.984	1.013	2.0
Y01-52-2	0.273	0.367	0.289	0.107	0.001	0.007	1.044	0.003	1.026	0.971	2.0
Y01-57-1	0.222	0.419	0.276			0.004	0.921	0.004	0.984	1.012	2.0

Y01-45-1 → 3 are measured on a single crystal, and Y01-47-14 → 17 are measured on another single crystal. Position of the sample: M: margin of the grain, C: core of the grain. Compositions are first quoted in weight %, then in atoms per formula unit.

Sb, and 0.3–1.5% Rh (Figs. 5A, B, Table 4). X-ray images show a uniform distribution of As, but a variable distribution of Sb (Fig. 5C).

Testibiopalladite is creamy white with a tinge of gray and generally has a diameter of  $10 \times 15 \mu\text{m}$ , but may be up to  $50 \times 80 \mu\text{m}$ . It has either an anhedral or roundish shape (Figs. 6A, B) where enclosed in pyrrhotite and pentlandite grains, or a lenticular shape where found between two crystals of pyrrhotite (Fig. 5C). Testibiopalladite contains 24.6–26.4% Pd, 32.4–37.2% Te, 14.3–19.7% Bi, and 20.7–22.8% Sb (Table 5). Spot analyses on single grains (Y01-56-4, -5, and -6; Y01-47-8 and -9) indicate that the testibiopalladite is rather homogeneous. It was reported to have the chemical formula Pd(Sb,Bi)Te or PdSbTe by Chao & Cabri (1976) and Cabri (1981b), respectively, in which up to 50% Bi can substitute for Sb (Kim & Chao 1991). Values of the Bi:Sb ratio less than 1 (Table 5) show that Bi does substitute for Sb in testibiopalladite.

Only a few anhedral grains of milk-white melonite, embedded in pyrrhotite and pentlandite grains, are found in massive ore samples (Fig. 5D). Their appearance is similar to that from the South Range at Sudbury (Cabri & Laflamme 1976). The melonite from Yangliuping contains 10.6% Pd and 10.8% Ni, with a Ni:Pd atomic ratio of 1.83 (Table 5). The Pd-bearing melonite contains slightly higher Bi (8.6%), lower Sb (1.3%) and Te (67.5%) (Table 5) than testibiopalladite.

The PGM species and their textural relations with BMS in massive ores from the Yangliuping deposit are similar to those in sulfide ores from the South Range at Sudbury (Cabri & Laflamme 1976), but obviously different from those of the Bacuri complex, Amapa, Brazil (Prichard et al. 2001). In the South Range at Sudbury, the PGM include tellurides, arsenides, and antimonides (Cabri & Laflamme 1976). In contrast, in the serpentized Bacuri complex, Amapa, Brazil, the most common PGM are Pd bismuthides, sperrylite, laurite and

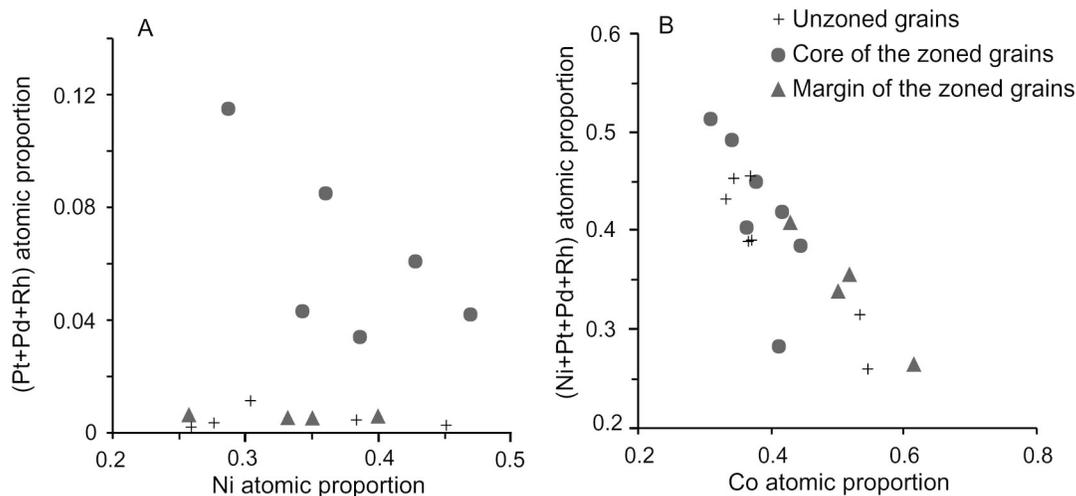


FIG. 4. A. Correlation between (Pt + Pd + Rh) and Ni in cobaltite-gersdorffite solid solution. The atomic proportions of (Pt + Pd + Rh) in the cores of the cobaltite-gersdorffite solid solution grains with compositional zones correlate negatively with Ni. Those proportions in the margin of the zoned grains of cobaltite-gersdorffite solid solution and of the grains without compositional zones are relatively low. B. The atomic proportions of (Ni + Pt + Pd + Rh) also correlate negatively with Co.

TABLE 4. COMPOSITION OF SPERRYLITE FROM THE MASSIVE ORES OF THE YANGLIUPING DEPOSIT, SOUTHWESTERN CHINA

Sample	Position	Fe	Rh	Pt	Pd	As	Sb	S	Total	Fe	Rh	Pt	Pd	$\Sigma$	As	Sb	S	$\Sigma$
Y01-39-1	C	0.2		55.7		40.5	2.1	0.1	98.8	0.013		1.018		1.032	1.927	0.061	0.012	2
Y01-39-8	C	0.2	0.3	54.5		44.3	1.1	0.2	100.8	0.011	0.011	0.920		0.942	1.951	0.031	0.019	2
Y01-39-2		0.2	1.5	52.3	0.0	44.6	1.3	0.3	100.5	0.012	0.049	0.871	0.000	0.932	1.934	0.034	0.032	2
Y01-39-3		0.1	1.0	54.2	0.1	41.2	2.0	0.3	99.1	0.008	0.035	0.964	0.003	1.010	1.909	0.058	0.032	2
Y01-39-4		0.2	0.9	54.2	0.1	40.7	1.7	0.3	98.2	0.014	0.031	0.982	0.002	1.028	1.922	0.050	0.028	2
Y01-39-5	M	0.4	0.9	53.4		41.0	2.0	0.3	98.3	0.024	0.032	0.957		1.013	1.916	0.057	0.027	2
Y01-39-11	C	0.3	0.3	55.4		41.3	1.2	0.2	98.7	0.018	0.010	1.004		1.032	1.948	0.034	0.018	2
Y01-39-12		0.3	1.0	55.1		41.8	1.4	0.2	100.0	0.017	0.034	0.982		1.033	1.940	0.041	0.020	2
Y01-39-13	M	0.7	0.9	55.2		41.7	1.6	0.2	100.4	0.040	0.031	0.982		1.054	1.933	0.046	0.021	2

Y01-39-1 → 5 and 8 are measured on a single crystal, and Y01-39-11 → 13 are measured on another single crystal. Position of the sample: M: margin of the grain, C: center of the grain. Compositions are first quoted in weight %, then in atoms per formula unit.

irarsite, which were formed during alteration; they are devoid of regular compositional zones, and occur as irregular inclusions in alteration silicates (Prichard *et al.* 2001).

#### PARAGENESIS OF THE MINERALS

##### *PGE in solid solution in Mss*

The exsolution of pentlandite from pyrrhotite in the massive ores of the Yangliuping deposit (Figs. 2A, B) suggests that monosulfide solid-solution (*Mss*) crystallized from sulfide melts possibly over a range of temperatures from 1100° to 800°C according to the

experimental data for the system Fe-Ni-S (*e.g.*, Craig & Scott 1973, Kelly & Vaughan 1983, Kullerud *et al.* 1969, Naldrett *et al.* 1967, Naldrett 1969, Misra & Fleet 1973, Craig 1981). Progressive exsolution of pentlandite resulted in Ni zonation in pyrrhotite crystals from the margin toward the center (Table 1).

The concentrations of Pt in pyrrhotite and pentlandite are highly variable, ranging from below detection limit to 0.5 wt% (Table 1). About 30% of all points analyzed show Pt at a level between 0.1 and 0.5 wt% Pt. The partition coefficients of Pt between *Mss* and sulfide liquid are generally less than 0.24 (Fleet *et al.* 1993, Li *et al.* 1996, Barnes *et al.* 1997, Barnes & Maier 1999); if Pt existed in the pyrrhotite structure as a solid-solu-

TABLE 5. CHEMICAL COMPOSITION OF TESTIBIOPALLADITE AND MELONITE FROM THE MASSIVE ORES OF THE YANGLIUPING DEPOSIT, SOUTHWESTERN CHINA

Sample	Position	Fe	Cu	Ni	Pt	Pd	Sb	Bi	As	Te	Se	Total		
<b>Testibiopalladite</b>														
Y01-56-4	C	0.2	0.1	0.5	0.5	26.2	21.0	19.7	0.2	32.9	0.1	101.4		
Y01-56-5	C	0.3	0.1	0.3	0.3	25.9	21.6	18.7	0.2	32.4	0.0	100.0		
Y01-56-6	M	0.4		0.5	0.4	26.4	21.8	17.1	0.2	33.5	0.1	100.6		
Y01-47-8	C	0.4		1.4		25.4	22.6	14.3	0.3	35.8	0.1	100.9		
Y01-47-9	C	0.4		1.5		25.0	22.8	14.4	0.3	36.1		100.6		
Y01-47-10	M	0.7	0.1	1.1		24.6	20.7	15.6	0.2	37.2		100.2		
<b>Melonite</b>														
Y01-47-4		0.6		10.8		10.6	1.3	8.6		67.5		99.6		
Sample		Fe	Cu	Ni	Pt	Pd	Σ	Sb	Bi	As	Σ	Te	Se	Σ
<b>Testibiopalladite</b>														
Y01-56-4		0.014	0.004	0.034	0.009	0.950	1.011	0.665	0.363	0.010	1.038	0.995	0.005	1.000
Y01-56-5		0.021	0.007	0.017	0.007	0.957	1.010	0.684	0.345	0.010	1.040	0.999	0.001	1.000
Y01-56-6		0.027		0.030	0.008	0.942	1.008	0.691	0.315	0.011	1.018	0.997	0.003	1.000
Y01-47-8		0.023		0.087		0.849	0.958	0.716	0.264	0.016	0.996	0.996	0.004	1.000
Y01-47-9		0.023		0.091		0.832	0.946	0.723	0.265	0.013	1.002	1.000		1.000
Y01-47-10		0.043	0.003	0.067		0.793	0.906	0.656	0.288	0.008	0.952	1.000		1.000
<b>Melonite</b>														
Y01-47-4		0.033		0.631		0.344	1.009	0.037	0.141			1.821		2.000

Y01-56-4 → 6 are measured on a single crystal, and Y01-47-8 → 10 are measured on another single crystal. Position of the sample: M: margin of the grain, C: center of the grain. Compositions are first quoted in weight %, then in atoms per formula unit.

tion component, the parent sulfide melt would be expected to contain at least 0.42–2.08 wt% Pt. It is unlikely that a natural sulfide melt contains such a high proportion of PGE. Thus, Pt must exist in the pyrrhotite as invisible discrete PGM inclusions, rather than as a solid-solution component. Therefore, the discrete inclusions of PGM probably formed at the boundary of pyrrhotite grains, where the PGE became concentrated in the residual sulfide melt as the pyrrhotite crystal grew. The discrete inclusions of PGM then were engulfed by the growing grains of pyrrhotite. Pt in pyrrhotite and pentlandite thus mostly occurs as submicroscopic inclusions of Pt minerals, similar to the case in sulfide ores from Sudbury (Li *et al.* 1993). Zientek & Oscarson (1987) identified such discrete inclusions of PGM in pentlandite crystals containing 37 ppm Pd and 55 ppm Pt by scanning electron microscopy.

#### *Origin of cobaltite–gersdorffite solid solution*

The Pd- and Rh-bearing cobaltite–gersdorffite solid solution in the massive ores may have crystallized directly from a sulfide melt. Evidence for a magmatic ori-

gin includes: 1) well-developed growth-related compositional zones parallel or subparallel to crystal faces (Figs. 3A, B), 2) lack of alteration of the early-formed zones, and 3) cryptic compositional zoning that is consistent with crystallization (Fig. 6). Sulfarsenide grains with iridarsenide – irarsite – hollingworthite – nickeloan cobaltite assemblages show typical compositional zones from the core to the edge in the Hitura nickel deposit in Finland (Häkli *et al.* 1976). Other examples of concentric compositionally zoned sulfarsenide are found in typical magmatic sulfide ores from the Las Aguilas Ni–Cu deposits of Argentina (Gervilla *et al.* 1997) and the Mount General'skaya layered intrusion, Russia (Barkov *et al.* 1999). In contrast, sulfarsenide grains from hydrothermal deposits are distinctive, with irregular and complex compositional zoning (*e.g.*, Ohnenstetter *et al.* 1991).

The correlations between (Pt + Pd + Rh) and Ni and between (Ni + Pt + Pd + Rh) and Co (Figs. 4A, B) indicate that Fe, Pt, Pd, and Rh substitute for Co and Ni in the core of the cobaltite–gersdorffite solid solution. Atoms of Fe have a smaller covalent radius (1.23 Å) than Co (1.32 Å) and Ni (1.39 Å), and Pt, Pd, and Rh have

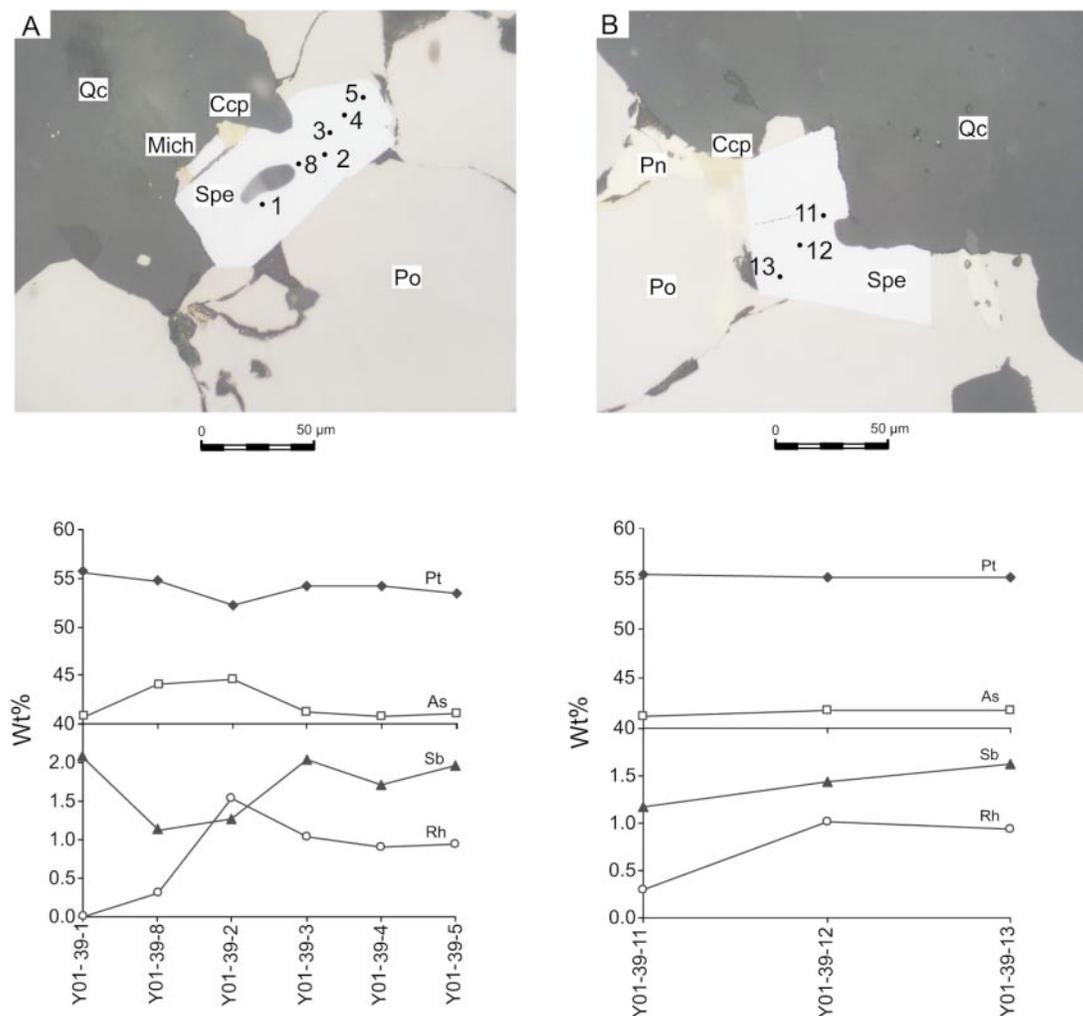


FIG. 5. A. and B. Subhedral grains of sperrylite, embedded in pyrrhotite, appear to have been dissolved by late hydrothermal fluids. Compositional data are presented in Table 4. Po: pyrrhotite; Pn: pentlandite; Ccp: chalcopyrite; Spe: sperrylite; Qc: quartz and calcite; Mich: michenerite.

higher electronegativities ( $\sim 2.2$ ) than Co and Ni ( $\sim 1.8$ ) (Evans 1996). The substitution of Fe, Pt, Pd, and Rh for Co and Ni can stabilize the structure of the cobaltite–gersdorffite solid solution. Thus, Pt + Pd + Rh may be added to the FeAsS end-member in the system FeAsS – NiAsS – CoAsS (Klemm 1965). Figure 7 also suggests that cobaltite–gersdorffite solid solution crystallized at temperatures between 650° and 600°C, higher than the temperature of initial exsolution of pentlandite from *Mss* (Kelly & Vaughan 1983).

#### Origin of the PGM

Sperrylite, testibiopalladite, and Pd-bearing melonite occur most commonly as inclusions in pyrrhotite and pentlandite crystals or between crystals of pyrrhotite (Fig. 6). The textural relations between PGM and BMS suggest that they are of magmatic origin, rather than of hydrothermal origin.

Pt and Pd are incompatible in *Mss*, and their *Mss*–melt partition coefficients decrease with decreasing tem-

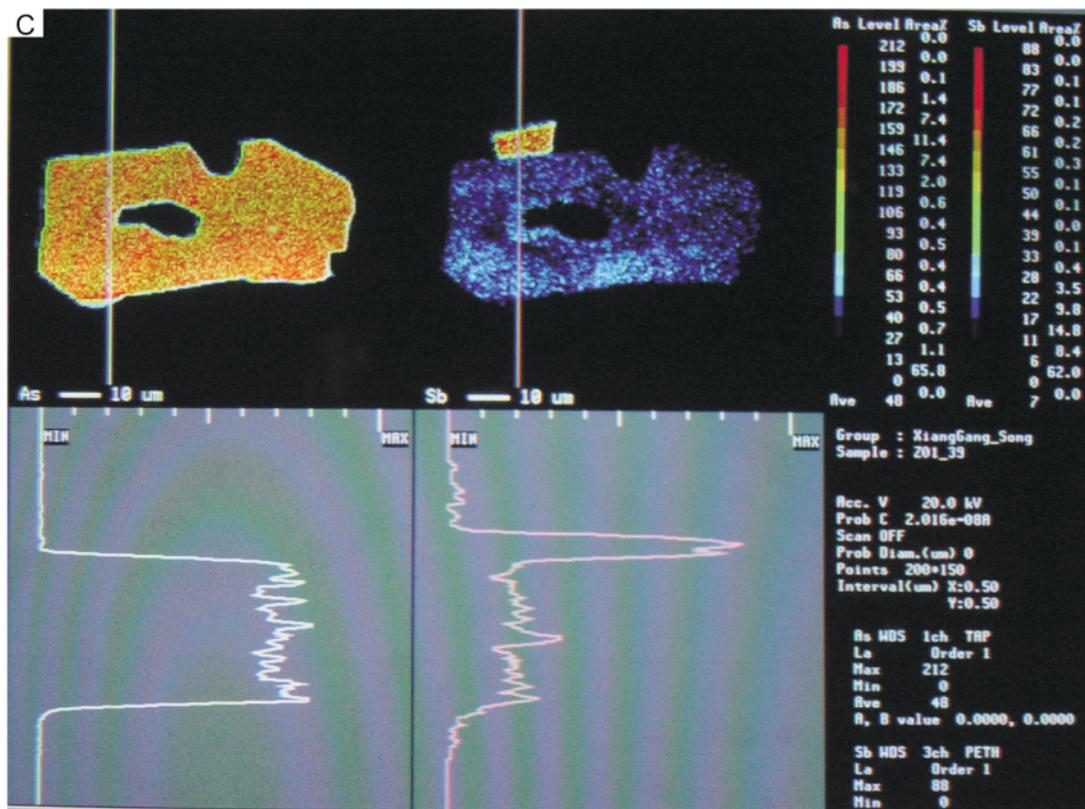


FIG. 5. C. X-ray area scans and compositional sections of As and Sb for the sperrylite grain shown in A. As contents in the sperrylite grain are uniform, and the Sb contents are erratic. Compositional data are presented in Table 4 (Y01-39-1 to -5 and -8, and Y01-39-11 to -13).

perature (Fleet *et al.* 1993, Li *et al.* 1996, Barnes *et al.* 1997). The presence of submicroscopic inclusions of PGM in pyrrhotite and pentlandite in the massive ores is consistent with exsolution of PGM from the *Mss* structure on cooling. As *Mss* crystallized, Pt and Pd became more concentrated in the residual liquid, and eventually bonded with As, Te, Sb, or Bi in the residual liquid to form sperrylite, testibiopalladite, and Pd-bearing melonite. The experimental results in the systems Pt-Pd-Fe-As-S and Pd-Sb-Te indicate that arsenides, sulfarsenides, and Sb tellurides of PGE, such as iridarsenide, irarsite, hollingworthite, testibiopalladite, sperrylite, omeiite, and sudburyite, can crystallize from an As- and Sb-bearing liquid (Cabri & Laflamme 1976, Skinner *et al.* 1976, Kim & Chao 1991, Makovicky *et al.* 1990, 1992, Fleet *et al.* 1993). As, Sb, and Te may become enriched in the residual liquid of a magmatic sulfide melt or as a result of assimilation of country-rock-derived constituents. Proton-microprobe studies

show that small quantities of As, Sb, Te, and the PGE occur in solid solution in magmatic BMS in the Noril'sk-Talnakh ores (Lightfoot *et al.* 1994). A fraction of these elements may have been expelled from the sulfides to a residual liquid.

It is generally accepted that the PGM may have crystallized from residual liquids during fractional crystallization of sulfide melts (Naldrett & Barnes 1986, Cabri 1981a, Peach *et al.* 1990, Ebel & Naldrett 1997). Accordingly, the BMS and PGM in the massive ores of the Yangliuping deposit probably formed by fractional crystallization of a sulfide melt. Monosulfide solid-solution was the first phase to crystallize from the sulfide melt. The cobaltite-gersdorffite solid solution formed prior to the initial exsolution of pentlandite. Sperrylite, testibiopalladite, and Pd-bearing melonite crystallized at a later stage, at which point Pt, Pd, and As had become highly enriched in the residual sulfide liquid. On the basis of our new data, we propose that the PGM in

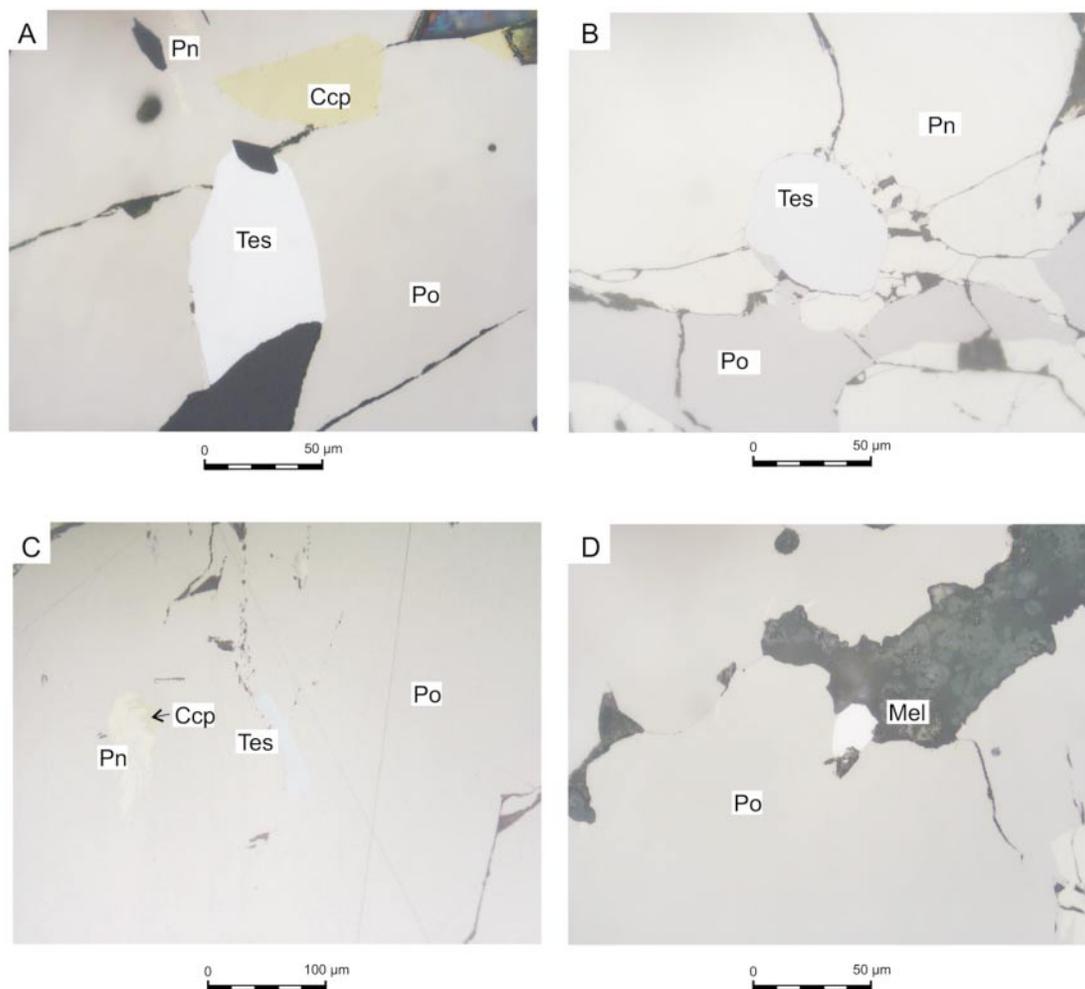


FIG. 6. A. Anhedronal grain of testibiopalladite embedded in pyrrhotite. B. Anhedronal grain of testibiopalladite embedded in pentlandite. C. Testibiopalladite on the margin between two grains of pyrrhotite. D. Pd-bearing melonite embedded in pyrrhotite and apparently dissolved by late hydrothermal fluids. Po: pyrrhotite, Pn: pentlandite, Ccp: chalcopyrite, Tes: testibiopalladite, Mel: melonite.

the massive ores of the Yangliuping Ni–Cu–(PGE) sulfide deposit crystallized as a result of progressive fractionation of the sulfide melt and exsolution of PGE from *Mss*. However, the potential contribution of PGE exsolution from *Mss* to the formation of PGM requires further study.

#### CONCLUSIONS

The principal conclusions of this study are as follows:

1. The Yangliuping Ni–Cu–(PGE) sulfide deposit has a magmatic origin and contains abundant BMS and PGM.
2. Sperrylite, testibiopalladite, and Pd-bearing melonite in massive ores formed during crystallization of *Mss* from a sulfide melt and its subsolidus re-equilibration.
3. Compositionally zoned PGE-bearing cobaltite–gersdorffite solid solution appeared prior to exsolution of pentlandite from *Mss*.

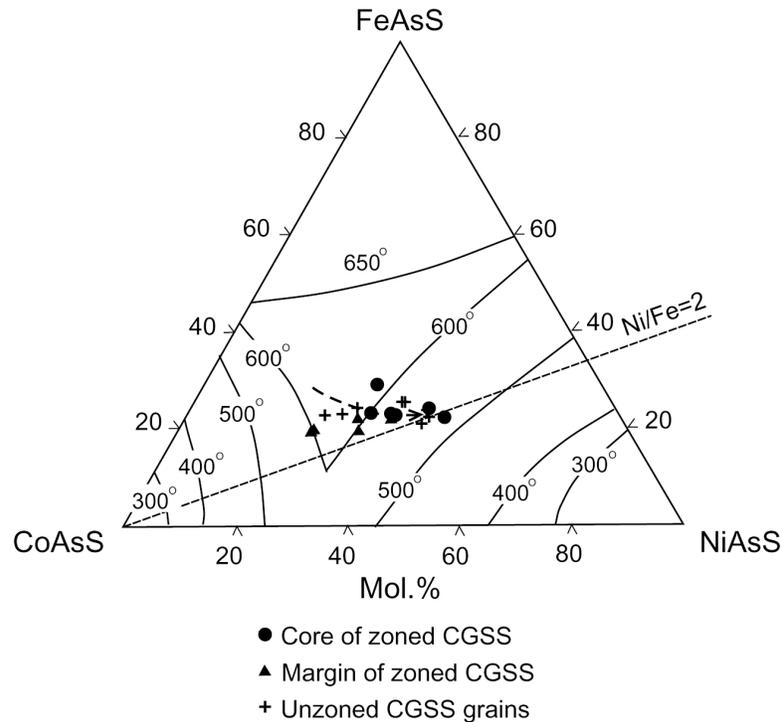


FIG. 7. Crystallization trend of the cobaltite-gersdorffite solid solution in massive ores in the Yangliuping deposit in terms of the system FeAsS – NiAsS – CoAsS (mol.%) (Klemm 1965).

4. Sperrylite, testibiopalladite, and Pd-bearing melonite crystallized from a residual fraction of the sulfide melt.

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