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IN SITU QUANTITATIVE ANALYSES FOR PGE AND Au IN SULFIDE MINERALS OF THE JINCHUAN Ni–Cu DEPOSIT BY ACCELERATOR MASS SPECTROMETRY

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ABSTRACT

Pyrrhotite, pentlandite and chalcopyrite from the Jinchuan Ni–Cu deposit, China, have been analyzed for the first time for all PGE and Au, using *in situ* accelerator mass spectrometry (AMS). Trace amounts of Pt (0.07–2.2 ppb) were detected in all three minerals. These contents are much lower than the whole-rock concentrations of Pt, which attain several ppm. Iridium content of the minerals falls between 1.7 and 37 ppb, which is generally less than half of the whole-rock concentrations. Os, Ru and Rh contents in these sulfide minerals increase in the order: chalcopyrite, pyrrhotite, pentlandite. Pentlandite can normally account for up to 46% of the Os, Ru and Rh of the sulfide ores, and the abundances of these elements in pentlandite increase with those of the whole rock. Pentlandite is enriched in Pd (122–6362 ppb) by up to 20 times the whole-rock concentrations. A good linear relationship is observed between the Pd content of pentlandite and that in 100% sulfide, suggesting that equilibrium was reached during the exsolution of pentlandite from monosulfide solid-solution (*Mss*), and that Pd is structurally bound. Pyrrhotite and chalcopyrite contain much less Pd than pentlandite and the whole rock, indicating that they are not important Pd carriers. Au invariably is low in the sulfide minerals, probably reflecting its preference for the liquid phase during crystallization of the sulfide melt. Enrichment of Pd, Os, Ru and Rh, and depletion of Pt, Au and Ir, in the sulfide minerals suggest that the first four PGE probably existed as metal sulfides, which tend to enter the *Mss*, whereas the other three elements remained as stable metals that preferred the liquid during the crystallization of sulfide melt. The data have also demonstrated the great potential of accelerator mass spectrometry in the study of the geochemistry of PGE and the metallogenesis of Ni–Cu–PGE sulfide deposits.

Keywords: Jinchuan Ni–Cu deposit, platinum-group elements, accelerator mass spectrometry, monosulfide solid-solution, pentlandite, chalcopyrite, pyrrhotite, China.

SOMMAIRE

Nous avons déterminé, pour la première fois, la teneur en éléments du groupe du platine et en or d'échantillons de pyrrhotite, pentlandite et chalcopyrite provenant du gisement à Ni–Cu de Jinchuan (Chine); nous nous sommes servis d'un accélérateur *in situ* avec spectromètre de masse. Avec cette technique, nous avons pu déceler le Pt au niveau de traces (0.07–2.2 ppb) dans les trois minéraux. Ces niveaux sont de beaucoup inférieurs aux concentrations dans les roches totales, qui atteignent plusieurs ppm. La teneur en iridium des trois minéraux se situe entre 1.7 et 37 ppb, ce qui correspond à moins de la moitié de sa concentration dans les roches totales. Les teneurs en Os, Ru et Rh augmentent dans l'ordre chalcopyrite, pyrrhotite, pentlandite. Cette dernière peut contenir jusqu'à 46% de ces trois éléments dans le minerai sulfuré; la concentration de ces éléments dans la pentlandite augmente avec leur concentration dans les roches totales. La pentlandite est enrichie jusqu'à 20 fois en Pd (122–6362 ppb), par rapport aux roches totales. Nous trouvons une bonne corrélation linéaire entre la quantité de Pd dans la pentlandite et dans la fraction sulfurée de la roche; l'équilibre aurait donc été atteint lors de l'exsolution de la pentlandite d'une solution solide monosulfurée (*Mss*), et le Pd résiderait alors dans la structure de la pentlandite. Pyrrhotite et chalcopyrite contiennent beaucoup moins de Pd que la pentlandite et la roche totale; ils ne semblent pas être des hôtes importants du Pd. La teneur en or des sulfures est très faible, résultat probable de sa préférence pour la phase liquide silicatée lors de la cristallisation du liquide sulfuré. D'après l'enrichissement des sulfures en Pd, Os, Ru et Rh, et leurs faibles teneurs en Pt, Au et Ir, nous pensons que les quatre premiers éléments auraient existé sous forme de sulfures, et donc incorporés à la phase *Mss*, tandis que les trois autres seraient restés stables à l'état métallique, préférant le liquide silicaté pendant la cristallisation du liquide sulfuré. Les données illustrent bien le vaste potentiel de la méthode analytique nouvelle pour l'étude de la distribution des éléments du groupe du platine et de l'origine des gisements de sulfures qui concentrent ces éléments, le Ni et le Cu.

(Traduit par la Rédaction)

Mots-clés: gisement à Ni–Cu, Jinchuan, éléments du groupe du platine, accélérateur avec spectromètre de masse, solution solide monosulfurée, pentlandite, chalcopyrite, pyrrhotite, Chine.

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INTRODUCTION

Concentrations of the platinum-group elements (PGE) are commonly associated with Ni–Cu sulfide mineralization in mafic–ultramafic intrusions. Although the levels of PGE enrichment vary with different host-rocks and different amount of sulfides in the ore, these elements are invariably associated with sulfide minerals. Thus, the occurrence of PGE and their relationship with the sulfide minerals are very important in understanding the process of PGE mineralization.

Detailed mineralogical studies on platinum-group minerals (PGM) have provided a good understanding of the distribution of the PGE in sulfide ores and their geochemistry during sulfide mineralization (Vermaak & Hendriks 1976, Cabri & Laflamme 1981, McLaren & De Villiers 1982, Sweeny & Edgar 1988), but problems remain as to the importance of sulfide minerals in dissolving PGE and the exact siting of these elements, due to the difficulties of direct determination of PGE in sulfide minerals and of quantitative estimation of platinum-group minerals (PGM) on account of their heterogeneous distribution in most sulfide ores.

A quantitative estimate of PGE distribution in sulfide ores depends on precise *in situ* analyses of sulfide and other minerals. Previously, the electron microprobe was used for *in situ* analyses of PGE in sulfides, and detection limits of 100 ppm were commonly obtained. Other instruments, such as the ion microprobe (Lieble 1975, Cabri & Laflamme 1976) and the laser probe (Hillenkamp *et al.* 1975), also have been adopted, but the background of the spectrum has limited the sensitivity and maintained the detection limit at 100 ppm or slightly below (Chryssoulis *et al.* 1989). Consequently, except for Pd in sulfides from the PGE-rich deposits (Cabri *et al.* 1984, Genkin *et al.* 1973), most other PGE in sulfide minerals cannot be determined by the above techniques. It is not well known whether the PGE occur mainly as PGM in the sulfide ores or are structurally bound in the major sulfide minerals in Ni–Cu–PGE deposits.

During the last decade, accelerator mass spectrometry (AMS) has been found useful in analysis of trace amounts of heavy elements in solid phases (Rucklidge *et al.* 1982, Kilius *et al.* 1990). AMS has an effective molecular rejection through changes in the charge and molecular dissociation accomplished by the acceleration process. Also, because of the high energies used for particle detection, there is no complication due to dark current, *i.e.*, the background is negligible. Therefore, AMS can detect heavy elements down to ppb to sub-ppb levels in single grains in polished sections (Rucklidge *et al.* 1990, Kilius *et al.* 1990). There are limitations to this technique: it is destructive to the sample, and the primary beam for analysis usually has a diameter greater than 0.5 mm, which commonly is larger than the grain size of the sulfide minerals.

In this study, AMS is used for the first time to determine concentrations of all the PGE and Au directly in the main sulfide minerals (pyrrhotite, pentlandite and chalcopyrite) of magmatic sulfide ores from the Jinchuan Ni–Cu deposit, China. The objectives of the study were: 1) to investigate the distribution of PGE and Au in these minerals and their relative importance in concentrating the PGE, 2) to estimate the relative proportions of PGE in solid solution in sulfides and as independent PGM in the sulfide-bearing rocks, and 3) to evaluate the potential of AMS for quantitative *in situ* determination of concentrations of the precious metals in the ore minerals.

OUTLINE OF THE GEOLOGY AND MINERALIZATION OF THE JINCHUAN DEPOSIT

The Jinchuan deposit is a huge accumulation of Ni–Cu sulfides in a dyke-like intrusion of ultramafic rocks, mainly peridotite and dunite (Chai & Naldrett 1992). The PGE and Au constitute an economically important component to the sulfide ores (S.G.U. 1984, Sun 1986). Sulfide mineralization occurs as concordant lenses in the lower central part of the intrusion (Fig. 1). Three types of ores are observed: net-textured (1–4 wt.% Ni), disseminated (0.5–1 wt.% Ni) and massive (>4 wt.% Ni). Net-textured ore occurs at the base of the intrusion or in the core of the ore lenses. Sulfides occur interstitial to the cumulus olivine and connect to each other, forming an evenly distributed network. Disseminated ore usually appears on top of the net-textured ore or as envelopes to the latter. Sulfides occur as discrete aggregates in the interstitial voids of the cumulus olivine. Massive sulfides are rare and occur locally as veins up to two meters thick, cross-cutting other ores and nearby country-rocks (S.G.U. 1984). Zones of PGE enrichment (either Pt or Pd, >1 ppm) have been found widely distributed in the lenses of sulfide ore, but the massive sulfides are usually depleted in PGE (Chai & Naldrett 1990).

The sulfide mineralogy is dominated by pyrrhotite, pentlandite (violarite), chalcopyrite, cubanite, mackinawite and pyrite, in order of decreasing abundance. Pyrrhotite occurs mainly as anhedral or subhedral crystals, with grain sizes ranging from 0.1 to 3 mm. Pentlandite is invariably associated with pyrrhotite and commonly forms subhedral to euhedral crystals (0.1–2 mm) enclosed within anhedral pyrrhotite; rarely, exsolution flames of pentlandite occur at the boundaries or in the fractures of pyrrhotite crystals. Violarite usually replaces pentlandite in the upper part of the deposit as very fine grains either along the cleavages, giving rise to a regular framework in the pentlandite crystals, or around their grain margins. Chalcopyrite mostly occurs as anhedral crystals disseminated within other sulfides or as very fine veinlets that cross-cut the silicate grains. In some of the massive ore, fragments of pyrrhotite and pentlandite are included within the chalcopyrite-dominant groundmass. Cubanite usually occurs as small lamellae with chalcopyrite; occasionally, it replaces

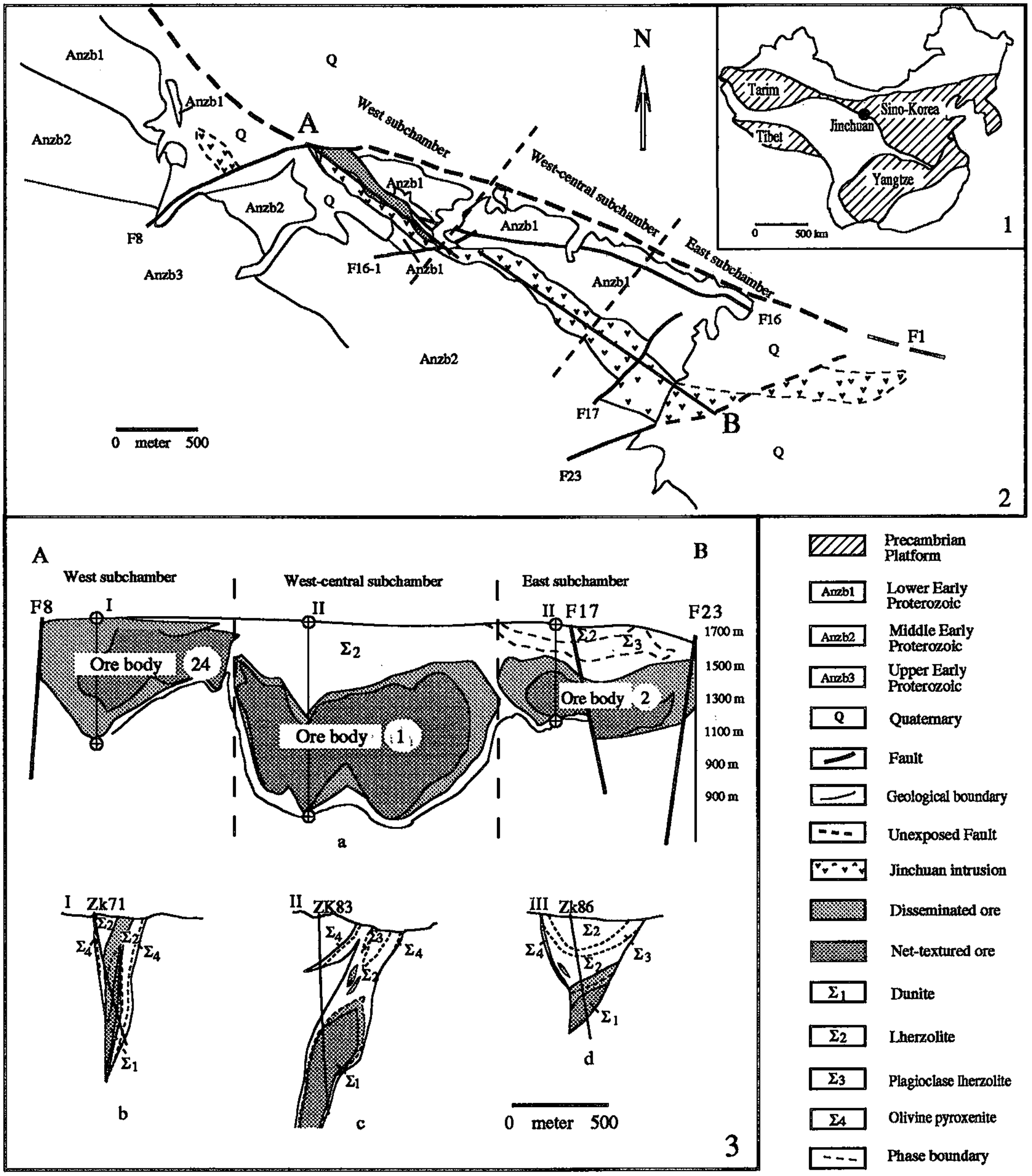

FIG. 1. Location, geological map and sections of the Jinchuan Ni–Cu deposit. (1) Location of the deposit in relation to the geological setting of China, (2) Surface geology, (3) Longitudinal and cross sections, a) longitudinal section, b) cross section of west subchamber, c) cross section of west-central subchamber, d) cross section of east subchamber. Data compiled from S.G.U. (1984) and Chai & Naldrett (1992).

pentlandite along its cleavages or fractures. Mackinawite generally occurs in pyrrhotite and pentlandite as various irregularly shaped bands or patches. More than ten PGM are reported to be associated with sulfide minerals (S.G.U. 1984). Sperrylite ($PtAs_2$) is the dominant PGM; it occurs as euhedral crystals (0.005–0.2 mm) at the boundary of pentlandite, chalcopyrite and pyrite, or within chalcopyrite and cubanite. Other PGM include native platinum, moncheite ($PtTe_2$), AuPtPd, melonite $(Ni,Pd,Pt)(Te,Bi)_2$, michenerite PdBiTe, and sudburyite (Pt,Pd)Sb (S.G.U. 1984).

SAMPLE PREPARATION AND ANALYTICAL PROCEDURES

Seven polished sections were chosen from relatively coarse-grained samples of the sulfide ores (with sulfide grains coarser than 0.5 mm, the size of the AMS ion beam normally used in the Isotrace Laboratory at the University of Toronto). Eight core cylinders (4 mm in diameter) were drilled from the polished sections, and two were taken from the same sample. Nine grains of pentlandite, three grains of pyrrhotite, and two grains of chalcopyrite were selected as analytical targets. The cylinders were mounted on a multiple aluminum holder capable of taking 12 separate cylinders. The remaining four spaces were taken by two cylinders of the SARM–7 standard, one of a Cu standard, and one of the standard MRB–9 (used to cross-check the measurements). The polished surfaces of the sample cores and standards were oriented parallel to the surface of the sample holder and were then mounted perpendicular to the Cs^+ beam, which minimizes scattering of the sputtered atoms.

Six of the ore samples selected were previously analyzed for whole-rock PGE using the Fire Assay Preconcentration and Neutron Activation method (Hoffman *et al.* 1978). The analytical results are listed in Table 1. Concentrations of Ni, Cu and S were determined by X-Ray Assay Laboratory, Don Mills, Ontario; these data were used to calculate the contents of sulfide minerals in the sample, based on the monosulfide method (Naldrett 1981). Knowledge of the sulfide content was required prior to making sulfide beads for the analyses of the whole-rock samples for the PGE. The calculated results of the contents of sulfide minerals and the content of total sulfide also are shown in Table 1.

SARM–7 was used as standard in analyses for the PGE in both the whole-rock samples by the neutron activation method and sulfide minerals by the AMS technique. In the AMS study, the standard was prepared by mixing the SARM–7 rock powder with sodium carbonate and tetraborate fluxes, Ni and S powders, and then heated to a high temperature (1000°C) to form a sulfide bead that concentrates the PGE in the standard (Hoffman *et al.* 1978). The sulfide bead was cut, polished on one surface and made into 4-mm cylinders as described above. Absolute errors based on counting statistics quoted for SARM–7 are expressed as a percentage of the mean, at the 95% confidence level, and range from 1.2% for Pt to 1.6% for Ir (Wilson *et al.* 1991). The maximum likely error in weighing the rock powders for bead preparation is less than 1%.

Sample heterogeneity is a potential problem, since the PGE may be present as small grains of alloy or sulfides, which may not be distributed evenly in a very tiny area. However, the 0.5-mm-diameter ion beam of the AMS is usually large enough to cover any heterogeneity in the bead. The mean standard deviations (% of mean) for 40 aliquots averaged about 2.5% for Pd, 6% for Au and 13% for Pt (Wilson *et al.* 1991). The relatively large scatter for Pt should be borne in mind in discussions of variations in AMS data. Two polished mounts of SARM–7, known to be homogeneous (G.C. Wilson, pers. comm.), were used as a double-check standard; one mount of the standard was analyzed before, and the second after the sample. Although a slightly finer beam (0.3–0.4 mm in diameter) was adopted in this study, reproducible analyses were still obtained from different locations across the standard. This indicates that the SARM–7 standard prepared by the fire assay method is sufficiently homogeneous for the purpose of AMS analysis.

The sample holder, mounted on an adjustable frame, was placed into the ion chamber, which was then evacuated to 10^{-6}–10^{-7} torr. The relative central spots of the mineral grains were chosen by a telemicroscope, which receives reflected light from an illuminator on the

TABLE 1. WHOLE-ROCK CONCENTRATIONS (ppb) OF THE PGE IN SELECTED SAMPLES

	2-35	II-W-9	II-W-15	II-W-22	2-E-5	II-25
Os	62.8	75.6	8.3	137.4	14.8	11.2
Ir	61.3	77	12.2	105.9	11.8	10.6
Ru	70.6	89.6	11.1	161.4	26.3	16.4
Rh	35.6	46.5	10.5	51.5	33.1	9.1
Pt	1514	147.3	107.4	2457.8	142.3	87
Pd	103	723.6	140.9	273.8	166.7	96
Au	33.4	185.5	258.8	140.8	197.8	123
Tpn	5.66	8.74	5.77	5.25	26.49	33.23
Tpo	12.37	12.61	9.94	20.24	29.28	42.36
Tcpy	0.43	6.18	4.2	1.25	18.46	24.64
Sulfides	18.46	27.53	19.91	26.74	74.23	100.23

Pn: Pentlandite Po: Pyrrhotite Cpy: Chalcopyrite Tpn: percentage of pn in whole rock.

other side of the sample chamber. Coordinates of these spots were recorded in the computer memory for automatic relocation. The mineral was bombarded by a 125–175 μA primary $^{133}Cs^+$ beam of 0.3–0.4 mm in diameter at a voltage of 30 kV. The sputtered ions were first selected for the desired mass, then accelerated in a Tandem accelerator at 2 MV terminal voltage. Acceleration of ions to 2 MV and a change in charge to the 6+ state ensure that there can be no molecular interferences, such as those that exist in the lower-energy secondary ion mass spectrometry (SIMS). The use of high-energy ions also results in the elimination of the dark current background normally present in SIMS. The resulting cations are detected by mass spectrometry. The counting time was set at 100 seconds per element, and an average of three analyses was taken for the final result. Since the ion beam erodes the samples quickly, the time selected for each run is a compromise chosen to minimize sample erosion and maximize sensitivity (Wilson *et al.* 1991).

RESULTS

The analytical results on the concentrations of PGE and Au in the sulfide minerals are presented in Table 2.

Pt, Ir and Au

Platinum contents range from 0.07 to 2.2 ppb in all sulfide minerals (Table 2). These are orders of magnitude lower than the corresponding whole-rock concentrations, indicating an almost complete absence of this element in the sulfide minerals. Despite the low concentration, the analytical values also show small deviations, suggesting both good reproducibility and a homogeneous distribution of Pt in the structure of these sulfide minerals.

Iridium content is usually low, ranging from 1.7 to 37 ppb. These values are generally less than half those of the corresponding whole-rock concentrations; exceptions are sample 2–E–5, in which chalcopyrite contains 12.6 ppb Ir and one pentlandite grain with a value of 29 ppb, which are both higher than the whole-rock concentration (11.8 ppb). Concentrations of Ir are very variable, both between samples, and between different grains of the same sample. The three grains of pentlandite of sample II–W–9 give two high values of 30 ppb and a low value of only 5 ppb, but individual grains all show good reproducibility. These data suggest that Ir is not only present in low concentrations, but that it is also distributed inhomogeneously in the sulfide minerals.

Gold is another element with a low concentration in the sulfide minerals. It ranges from a low of 0.2 ppb in pyrrhotite to a high of 28.6 ppb in pentlandite, and is usually between 1 and 5 ppb. In comparison to the whole-rock concentrations, Au is depleted at least ten times in the sulfide minerals. Samples with more than one grain of pentlandite give quite similar Au values, indicating that no discrete grains of Au-bearing alloy exist within this mineral.

Pd

The palladium content of the sulfide minerals ranges from ppb to ppm levels; Pd also shows the largest variation of all of the noble metals. Pentlandite has the highest contents, ranging from 122 to 6362 ppb. There seem to be two sets of samples: pentlandite in the massive sulfide samples has an appreciably lower Pd content than that in the net-textured ore (Table 2); two samples of massive sulfide have 100–300 ppb Pd in pentlandite, which is slightly higher than the corresponding whole-rock concentrations. In the remaining samples, which have lower sulfide contents (<28 wt.%), pentlandite contains 1087–6362 ppb Pd, much higher than the whole-rock concentrations. Some variation in Pd content is observed in different grains of pentlandite from the same sample, but these values are generally of the same order of magnitude. Three grains of pentlandite

TABLE 2. CONCENTRATIONS (ppb) OF THE PGE IN SULFIDE MINERALS

Sample	Mineral	Os	Ir	Ru	Rh	Pt	Pd	Au
II-25	Pentlandite	24 (8)	8.1 (1.2)	39 (39)	1.6 (0.3)	1.5 (0.8)	269 (20)	1.8 (0.1)
II-W-9(g1)		184 (16)	4.9 (0.6)	305 (30)	470 (35)	1.0 (0.5)	6217 (1480)	4.2 (0.1)
II-W-9(g2)		576 (16)	29.9 (1.2)	694 (129)	153 (7)	0.2 (0.07)	3313 (181)	0.4 (0.03)
II-W-9(g3)		96 (24)	29.9 (1.2)	406 (102)	90 (6.5)	(<0.07)	6362 (64)	8.6 (0.5)
2-35		547 (32)	26 (2.5)	5075 (2538)	3540 (1770)	0.5 (0.1)	1087 (214)	4.2 (0.1)
II-W-15		<7.7	9.0 (0.6)	13.5 (6.8)	63 (32)	0.2 (0.07)	2811 (985)	4.2 (0.1)
II-W-22		269 (7.9)	2.9 (0.5)	135 (34)	18.1 (4.2)	0.4 (0.1)	2311 (924)	22 (8)
2-E-5(g1)		16.3 (4.0)	1.2 (0.6)	40.6 (30.5)	2.9 (0.3)	0.15 (0.07)	276 (116)	23.5 (0.5)
2-E-5(g2)		105 (16)	29 (5)	20.3 (3.4)	12 (2)	<0.07	122 (3)	28.6 (0.3)
II-W-24	Pyrrhotite	32 (16)	32 (1.2)	27 (3)	32.9 (6.7)	2.2 (1.2)	802 (575)	1.4 (0.4)
2-35		643 (80)	26 (1.2)	271 (34)	2.9 (1.4)	<0.07	5.8 (2.9)	0.2 (0.1)
II-w-9		7.6 (0.5)	1.7 (0.2)	57.5 (16.9)	32 (3)	2.1 (0.7)	174 (29)	1.6 (0.1)
II-W-9	Chalcopyrite	72 (8)	37 (2.4)	<3.4	<0.3	0.6 (0.3)	13 (10)	4.2 (0.2)
2-E-5		78.5 (20)	12.6 (1.2)	13.5(6.8)	na	0.72 (0.07)	22.8 (10)	11.1 (0.3)

Numbers in parentheses are standard deviations. na: not available.

in sample II–W–9, for example, give two values of around 6500 ppb and one value of 3313 ppb. Thus, Pd can be considered to be reasonably evenly distributed in pentlandite. The Pd concentration in pentlandite of different ores seems to show an inverse correlation with the sulfide content of the ores (Fig. 2).

Three grains of pyrrhotite give Pd contents in the range of 5.8 to 802 ppb. Pyrrhotite from sample II–W–24 contains 802 ppb Pd, which is much higher than that of the other two samples. Since the whole-rock concentration of Pd for sample II–W–24 is not available, it is difficult to correlate Pd in pyrrhotite with the whole-rock concentration. Based on the other two values, the Pd content in pyrrhotite may increase with increase in whole-rock concentration, although, in general, it is much lower than that of the whole rock.

The two grains of chalcopyrite give Pd values of 13.0 and 22.8 ppb, which are also much lower than the corresponding whole-rock concentrations.

Os, Ru and Rh

Osmium content varies greatly, from less than 7.7 ppb to 643 ppb, in the three sulfide minerals. Generally, it is related to that of the whole rock, *i.e.*, the higher the whole-rock concentration, the higher the mineral content, but lower values also are observed. For example, pentlandite from sample II–W–15 contains less than 7.7 ppb Os, whereas the whole-rock sample gives 8.3 ppb Os, *i.e.*, higher than that of the mineral. Except for pentlandite from sample 2–35, which has an abnormally high concentration (547 ppb), the Os content of pentlandite increases with the Os content of the whole rock. Variations in Os content of different grains from the same sample also are presented. Two pentlandite grains from sample 2–E–5 give 16.3 and 105 ppb Os, and the three grains of pentlandite from sample II–W–9 have Os contents ranging from 96 to 576 ppb. These may reflect the existence of discrete Os-bearing PGM in the sulfide grains.

Ru is concentrated in both pentlandite and pyrrhotite at levels (>13 ppb) that exceed the whole-rock concentrations, but it seems to be depleted in chalcopyrite. Ru in pentlandite from sample 2–35 has an extremely high value (5075 ppb), orders of magnitude higher than the whole-rock concentration. This anomaly was probably caused by a small grain of a PGM in pentlandite, since we observed two high-mass counts (>720 c/s) before a low count (2.5 c/s) during the analyses, which may indicate that the PGM was eroded during the first two runs. Because of the destructive nature of the AMS method, three analyses were planned for each element at each spot, and no others were undertaken. The results presented here are an average of the three measurements. Similar to Ru, Rh also has an abnormal value (3540 ppb) in the same grain of pentlandite. The high values for both Ru and Rh may indicate that the PGM grain contains at least Ru and Rh, possibly Os, since an abnormally high Os value also was obtained in the same grain of pentlandite. Except for chalcopyrite, which contains almost no Rh, the Rh content in sulfide minerals is generally higher than that of the whole rock. The data also show large variations of Rh in different samples and in different grains of the same sample.

The concentrations of Os, Ru and Rh in different minerals (except for the pentlandite grain that has an abnormally high content of Ru and Rh) are plotted in Figure 3. This plot shows quite scattered distributions for the three elements in each mineral, from a low of near zero to a high of several hundred ppb, but it is nevertheless obvious that the concentrations of these elements in sulfide minerals are in the order pentlandite > pyrrhotite > chalcopyrite.

DISCUSSION

Pentlandite as the most important carrier of PGE

The AMS analyses establish that Pd, Rh, Ru and Os are generally enriched in pentlandite, whereas Pt, Au and Ir are strongly depleted in all the sulfide minerals. The

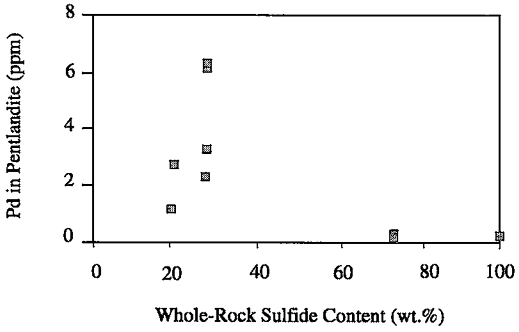

FIG. 2. Concentration of Pd in pentlandite in relation to sulfide content of the ores.

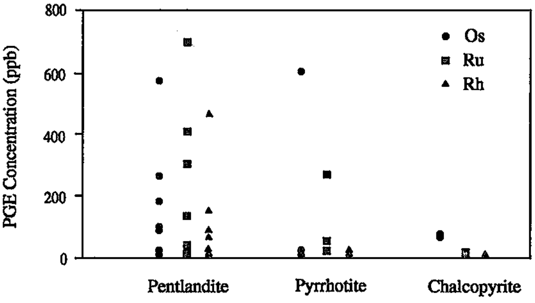

FIG. 3. Comparison of Os, Ru and Rh concentrations in sulfide minerals.

TABLE 3. ENRICHMENT FACTORS OF PGE IN SULFIDES OVER PGE IN WHOLE ROCKS

Sample	II-25	II-W-9	2-35	II-W-15	II-W-22	2-E-5	2-35	II-W-9	II-W-9	2-E-5
	Pentlandite						Pyrrhotite		Chalcopyrite	
Os	2.000	3.774	8.710*	0.928	1.958	4.098	10.239	0.101	0.952	5.304
Ir	0.540	0.280	0.424	0.738	0.027	1.280	0.424	0.022	0.481	1.068
Ru	1.393	5.227	71.884*	1.216	0.836	1.158	3.839	0.642	0.038	0.529
Rh	0.080	5.111	99.438*	6.000	0.351	0.225	0.081	0.688	0.006	<0.001
Pt	0.017	0.003	<0.001	0.002	<0.001	0.001	<0.001	0.014	0.004	0.005
Pd	2.802	7.321	10.553	19.950	8.440	1.632	0.056	0.240	0.018	0.137
Au	0.015	0.024	0.126	0.016	0.156	0.132	0.006	0.009	0.023	0.056

*: PGM inclusions present.

enrichment is also dependent on the whole-rock contents of sulfides and concentrations of the PGE. The enrichment factors (mineral/whole rock) of each PGE in different minerals are calculated and listed in Table 3.

Except for that from the massive sulfide ore, pentlandite shows Pd enrichment factors from 7 to 20, whereas pyrrhotite and chalcopyrite are depleted in Pd, with enrichment factors of less than 0.24. These results indicate that pentlandite is the only one of the three sulfide minerals studied that concentrates Pd.

Genkin *et al.* (1973) reported high concentrations of Pd in pentlandite (electron-microprobe data). They found Pd contents of 60–123 ppm in "flame" pentlandite that had exsolved from early pyrrhotite, and 32–59 ppm in "phenocryst-like" pentlandite.

Cabri & Laflamme (1976) used the ion microprobe to determine levels of PGE in the sulfides at Sudbury. Despite a detection limit at the 10 ppm level, Pt, Pd and Rh were not detected in pentlandite, pyrrhotite and chalcopyrite. They found 0.04–1.5 wt.% Pd in pentlandite from Stillwater (Cabri & Laflamme 1981). These data were confirmed by a subsequent investigation using the proton microprobe (Cabri *et al.* 1984).

Keays *et al.* (1981) studied Pd, Ir and Au concentrations in separates of sulfide minerals from the Ni deposits of the Kambalda camp. They obtained consistently high values of Pd (1.4 – 3.8 ppm) in pentlandite; Ir is more uniformly distributed, with higher values in pyrite, and chalcopyrite is the most important host for Au. Thus, they concluded that pentlandite is the dominant host of the Pd in these ores.

The results of the present study agree well with the above indications that pentlandite is the main carrier of Pd in magmatic sulfide deposits. Moreover, the Pd content of pentlandite seems related to that of the whole rock. The PGE-rich deposits at Stillwater have Pd concentrations of up to several hundred ppm (Barnes & Naldrett 1985), and the pentlandite there attains levels in excess of 1 wt.% Pd. On the other hand, less PGE-rich sulfide deposits, such as those of the Jinchuan and Kambalda Ni camps, contain pentlandite with Pd at the ppm level. The moderately high-Pd sulfide ores of the Noril'sk region (Genkin *et al.* 1973) contain pentlandite with Pd intermediate between that in the above two types of deposits. Therefore, Pd contents in pentlandite seem to be proportional to the whole-rock concentrations of Pd.

The two samples of massive sulfide from the Jinchuan deposit have whole-rock Pd contents of 96 and 166.7 ppb (Table 1), which are not necessarily lower than some of the other sulfide-bearing samples; however, pentlandite from these massive sulfides invariably contains lower Pd, generally about an order of magnitude lower, as demonstrated by its enrichment factors of 2–4 (Table 3). This finding suggests that the Pd content in pentlandite may not be directly related to its concentration in the sample itself but to that in the sulfides within the sample. This suggestion is reasonable since pentlandite is a product of exsolution from *Mss* (Craig & Scott 1974).

Based on this line of reasoning, Pd concentrations in the whole rocks are normalized to concentrations in 100% sulfide, then plotted against Pd contents in pentlandite (Fig. 4). For those samples from which more

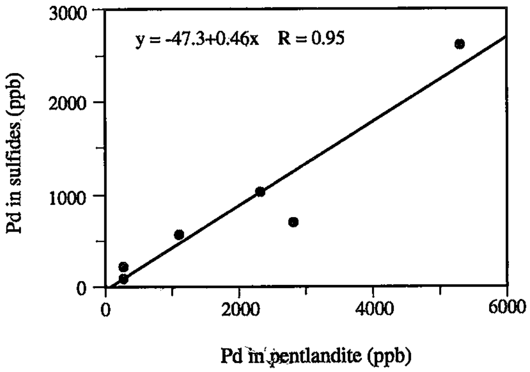

FIG. 4. Plot of Pd in pentlandite *versus* Pd in 100% sulfide, showing a good linear correlation. The concentrations of Pd are represented in ppb.

TABLE 4. PROPORTION OF PGE+Au IN SULFIDES IN RELATION TO THAT IN WHOLE ROCK

Sample	II-25	II-W-9	2-35	II-W-15	II-W-22	2-E-5	2-35	II-w-9	II-W-9	2-E-5
	Pentlandite						Pyrrhotite		Chalcopyrite	
Os	66.00	32.99	49.30	5.35	10.28	108.56	126.65	1.27	5.89	97.91
Ir	17.82	2.45	2.40	4.26	0.14	33.90	5.25	0.28	2.97	19.71
Ru	45.96	45.68	406.86	7.02	4.39	30.67	47.48	8.09	0.23	9.76
Rh	2.64	44.67	562.82	34.62	1.85	5.96	1.01	8.68	0.04	na
Pt	0.57	0.02	0	0.01	0	0.02	0	0.18	0.03	0.09
Pd	92.47	63.98	59.73	115.11	44.31	43.22	0.70	3.03	0.11	2.52
Au	0.48	0.21	0.71	0.09	0.82	3.49	0.07	0.11	0.14	1.04

than one grain of pentlandite was analyzed, average values are used. A very good linear relationship is observed, in which the Pd content of pentlandite increases with the concentration in the whole rock normalized to 100 wt.% sulfides. This linear relationship suggests that the Pd content in pentlandite reflects the equilibrium that was established during crystallization of the ore from a sulfide melt and the subsequent exsolution of pentlandite from *Mss*; it carries the implication that Pd was distributed by accommodation as a solid solution in pentlandite. The relatively uniform distribution of Pd within pentlandite grains from the same sample also suggests that diffusion of Pd through the monosulfide solid-solution was sufficiently rapid to permit equilibrium to be maintained during exsolution of pentlandite. The slope of the linear regression in Figure 4 reflects the partition coefficient of Pd between pentlandite and the *Mss*, which is about 2.2 for the Jinchuan sulfides (Fig. 4). Keays *et al.* (1981) reached similar conclusions in their study of Pd in sulfide separates in the Kambalda Ni deposits. However, our *in situ* measurements allow us to exclude the possibility that Pd is present in PGM grains accidently included in the mineral separates.

Os, Ru and Rh are generally enriched in pentlandite and, to some extent, in pyrrhotite. The enrichment factors are less than 10, generally between 1 and 6. This indicates that these PGE are enriched in sulfides, but that the enrichment is not as strong as in the case of Pd. Moreover, these PGE are hosted by both pentlandite and pyrrhotite, an indication of their different partitioning between pentlandite and *Mss*. The proportion of these three PGE lower than that of Pd in the sulfide minerals indicates that a greater proportion of these PGE may occur as discrete PGM in the ores or as solid solutions in olivine and chromite (Brügmann *et al.* 1987, Page & Talkington 1984). The very low concentrations of Pt, Ir and Au in sulfide minerals (with enrichment factors of less than 0.2) suggest that the sulfide minerals may not have incorporated these elements from the very start of sulfide crystallization.

In summary, the AMS study has revealed that high concentrations of the PGE exist in sulfide minerals at Jinchuan. Pentlandite is important as a carrier of Pd, Os, Ru and Rh; pyrrhotite may account for some of the Os, Ru and Rh in the sulfide ores. Chalcopyrite does not contain substantial amounts of PGE and Au. Platinum-group minerals probably account for most of the Pt, Au and Ir in the sulfide ores.

The importance of PGM

Despite the important enrichment of PGE in the sulfide minerals, pentlandite in particular, these cannot account for the PGE concentrations in the sulfide ores. PGE contributions from either silicate and chromite, which are considered to contain important amounts of Os, Ir and Ru (Brügmann *et al.* 1987, Crocket 1981, Agiorgitis & Wolf 1978, Page & Talkington 1984), or PGM have to be considered.

In the Jinchuan deposit, unmineralized rocks contain very low levels of the PGE (with Pt and Pd less than 20 ppb, and Os, Ru and Rh between 0.5 and 1 ppb; Chai & Naldrett, unpubl. data). Since these rocks also contain trace amounts of S (0.1 – 0.2 wt.%), the PGE concentrations cannot be contained completely in silicate minerals or chromite, which is ubiquitous in the Jinchuan rocks (Chai & Naldrett 1992). Thus the contribution of these minerals must be much less than the above values. On the other hand, the average content of olivine in the Jinchuan rocks is about 70% (S.G.U. 1984); thus even if all the whole-rock Os, Ru and Rh were concentrated in the olivine, their respective concentrations would still be lower than 1.3 ppb, which is more than 10 times lower than the values characteristic of the sulfide ores. In the massive sulfide ore, there is little or no olivine, and the PGE can only exist either in the sulfide minerals or as PGM. Therefore, most of the PGE other than what in the main sulfide minerals are not carried by silicate minerals.

The remaining possibility is that chromite acts as a carrier of the PGE in the Jinchuan ores. Crocket *et al.* (1976) analyzed spinel separates from the Merensky Reef, Bushveld Complex. They obtained a similar range of Pd and Ir in spinel to that in sulfide, and suggested that spinel may be another important carrier of PGE. Subsequent studies also indicated that, in some cases, Cr-rich spinel contains appreciable concentrations of Ir, Os and Ru (Oshin & Crocket 1981, Page & Talkinton 1984). Chai & Naldrett (1992) observed that chromite is generally evenly distributed in the Jinchuan rocks, ranging between 0.5 and 2 modal %. Since the chromite-bearing, sulfide-free rocks do not contain high levels of the PGE, the contribution of the chromite to the whole-rock PGE seems to be limited. Thus, chromite probably does not add greatly to the PGE content of the sulfide-bearing rocks. The above discussion led us to conclude, therefore, that those PGE that are not in sulfide minerals exist as PGM.

In order to evaluate the quantity of PGM in the sulfide ores, we have calculated the contribution of pentlandite, pyrrhotite and chalcopyrite to the total whole-rock PGE, based on the percentage of these minerals in the ores (Table 4).

Pt, Au and Ir are very depleted in the sulfide minerals; thus they must occur predominantly as PGM. Mineral-separation experiments on PGE-enriched parts of the Jinchuan deposit (Sun 1986) showed that sperrylite is commonly concentrated in the heavy-mineral separates; in one sample, which contains 81 ppm Pt, more than 50 wt.% of the amount of Pt in the whole rock can be accounted for by the sperrylite separates; AgAu and PtAu alloys have also commonly been found in the heavy-mineral fraction. The PGM and Au alloys generally appear as fine (0.005–0.5 mm) euhedral grains, and PGM–chalcopyrite aggregates also are commonly observed (Sun 1986). This association likely reflects the fact that chalcopyrite is the last major sulfide mineral to crystallize from the sulfide liquid (Naldrett 1966), and that Pt and Au may have remained in the liquid while *Mss* crystallized; Pt and Au thus end up in the liquid from which chalcopyrite also has crystallized. No Ir-bearing mineral has been observed in the heavy-mineral separates, but solution tests on Ir-rich ore have revealed that most of the Ir stayed in the residue, which indicates its possible existence as PGM (Sun 1986). It is possible that Ir-bearing PGM are too small in grain size to be separated from the ore. The low Ir content in sulfide minerals from this study adds support to the conclusion that Ir mainly exists as PGM, possibly metal alloys.

According to the calculation (Table 4), Os in sulfide minerals from some samples can account for more than 100 wt.% of its whole-rock concentration. This anomaly can be explained as a result of the heterogeneous distribution of Os in sulfide minerals, possibly due to the presence of Os-bearing PGM. Ru and Rh in sulfides can account for up to 46 wt.% of their whole-rock concentrations, if the samples with anomalous Ru and Rh values are excluded. The detection of the anomalous amounts of these elements in pentlandite suggests their existence as discrete PGM. In addition, the large variation of the elements in sulfide minerals also suggests that not all the PGE in sulfide minerals occur in solid solution, and that some of them may exist as discrete PGM. Unlike Pt and Au, which did not enter the sulfide minerals during crystallization of the sulfide melt, inclusions of Os-, Ru- and Rh-bearing PGM in the sulfides may contain PGE that originally existed in solid solution in sulfides, but exsolved from them during cooling or later metamorphism. The weak positive correlation between levels of these elements in pentlandite and those in the whole rock may indicate that equilibrium was attained during exsolution of pentlandite. The irregularities of the correlation may be due to analytical errors at low concentrations (Kilius *et al.* 1990), or to expulsion of a certain amount of these PGE from the pentlandite and pyrrhotite grains. Pd in pentlandite can account from 43 to 100 wt.% of the total Pd of the whole rock, with an average of about 70 wt.%, indicating that the majority of Pd in the ore is located in pentlandite. Small amounts of Pd in pyrrhotite and chalcopyrite also were detected. Therefore, only a very small portion of Pd exists as Pd-bearing PGM in the Jinchuan sulfide ores. More than ten Pd-bearing minerals were reported, among which are bismuthotelluride, bismuthinite, metal alloys and stibnite, in decreasing order, but Pd is usually not the main component of these minerals, and the amount of Pd-bearing PGM in the whole-rock has not been established clearly, owing to their scarcity and their development as tiny grains (S.G.U. 1984). The AMS results can thus explain the absence of major Pd-bearing PGM.

Genetic implications of PGE in sulfides

Although this is a preliminary study, and the number of samples analyzed is limited, the results, in particular, the Pd content in pentlandite and pyrrhotite, can still provide genetic information about the process of PGE mineralization.

Makovicky *et al.* (1986) have studied the solubility of PGE in base metal sulfides in the systems Fe–PGE–S and Cu–Fe–PGE–S. They found that at high fugacities of S, pyrrhotite dissolves 11 wt.% Pd, 1.2 wt.% Pt, 3.6 wt.% Ru and 44 wt.% Rh at 900°C. Fe-rich *Mss* is the first phase to crystallize from an Fe–Ni–Cu sulfide liquid (Kullerud 1967, Craig & Scott 1974), and it should behave like pyrrhotite in the Ni-free system. The PGE concentrations of the Jinchuan sulfide ores are generally less than 10 ppm, and the ores usually contain more than 10 wt.% sulfide; thus there is more than enough *Mss* to dissolve all of the PGE. However, the amount of PGE that can dissolve in *Mss* will depend on the partitioning of these elements between *Mss* and sulfide liquid. It is possible that all of the PGE partitioned into *Mss* and were in solid solution at high temperature.

Makovicky *et al.* (1986) also found that at 500°C, pyrrhotite dissolves only 0.4 wt.% Pd, undetectable amounts of Pt and Ru, and 6.7 wt.% Rh, and that pentlandite accommodates up to 12.5 wt.% Pd, 12.4 wt.% Rh, 12.9 wt.% Ru, but undetectable levels of Pt.

The absolute concentrations of PGE in the minerals cannot be compared directly to the PGE in the Jinchuan sulfides, since the latter are much lower than even the detection limits of the experiments. However, the experimental results show the relative importance of pyrrhotite and pentlandite in concentrating the PGE, and the effect of temperature on PGE solubility in sulfides. This has implications with respect to the present study. For example, the experiments show that pentlandite is much richer in Pd and Ru, but not in Rh, than the coexisting pyrrhotite, and that Pt solubility in both minerals decreases rapidly with decreasing temperature. Therefore, in the case of the Jinchuan *Mss*, when subsequent cooling led to the exsolution of pentlandite, Pd may have entered pentlandite, leading to a depletion in the associated pyrrhotite, consistent with results of our AMS analyses (Table 2).

It is seen from Table 4 that, overall, the base metal sulfides can account for much of the Os, Ru, Rh and Pd in a bulk sample of ore, but almost none of the Pt, very little of the Au and relatively little of the Ir.

Makovicky *et al.* (1986) found that at 900°C, Pt is distributed between coexisting pyrrhotite and sulfide liquid, but favors the liquid (6–15 wt.%) over the pyrrhotite (1.2 wt.%). This indicates that even at the beginning of sulfide crystallization, Pt is incompatible in the *Mss* relative to the sulfide liquid. Pentlandite, exsolving from the *Mss*, will thus be depleted in Pt. Most of the Pt is likely to remain in the sulfide liquid and form independent PGM at a late stage in the crystallization. The close association of sperrylite with chalcopyrite adds support to this hypothesis. The distribution of Au is also likely due to the same cause, but there are no experimental data bearing on the behavior of Au during crystallization of a sulfide melt.

The behavior of Ir in the Jinchuan ores is surprising, since it tends to follow Ru and Os during geochemical fractionation. Furthermore, Li *et al.* (1993) reported high concentrations of Ir plus Ru and Os in pyrrhotite that represents the low-temperature equilibration of early-crystallizing *Mss* at the Strathcona mine, Sudbury. Naldrett *et al.* (1992) noted that Ir partitioned strongly ($D_{Ir} = 3$) into *Mss* that crystallized from the sulfide liquid giving rise to the ores of the Noril'sk region. The low Ir values recorded in the Jinchuan pyrrhotite may be due to one of two reasons: (1) the Ir originally partitioned into *Mss* but has exsolved as discrete PGM during subsequent cooling or metamorphism, or (2) Ir partitioning between *Mss* and sulfide liquid is a function of the prevailing $f(S_2)$. The problem with the first explanation is one of explaining why Ir has not behaved in the same way at Sudbury as at Jinchuan.

With regard to the second explanation, *Mss* started to form at Jinchuan at a high temperature from a sulfide melt, which was itself in equilibrium with a silicate melt. The sulfur fugacity of a sulfide melt – silicate melt mixture is defined to a large degree by the activity of FeO in the silicate melt and the prevailing oxygen fugacity (Shima & Naldrett 1975). The $f(O_2)$ *versus* temperature path of a cooling mafic–ultramafic magma is considered to be close to that of the quartz–fayalite–magnetite buffer (Barnes *et al.* 1988). The study of Shima & Naldrett (1975) indicates that a $\log f(S_2)$ of –1 is a reasonable value to be expected for a sulfide melt starting to crystallize at 1150°C under these conditions. The *Mss* will therefore be crystallizing close to the $Ir–Ir_2S_3$ sulfidation curve (Fig. 5). Although this curve and the others in Figure 5 apply to native metals in equilibrium with sulfur, these curves give an idea of the relative "chalcophilicity" of these metals at magmatic temperatures. It is possible that at lower fugacities of sulfur, Ir, for which the sulfidation reaction requires a significantly higher sulfur fugacity than it does for Ru and Os, could be present in a sulfide melt in the native state, whereas Ru and Os were present in association with sulfur; under these circumstances, Ir might tend to favor the sulfide melt, and Ru and Os, the *Mss*. At a slightly higher fugacity of sulfur, all three metals could be associated with sulfur in the sulfide melt, and thus be compatible in *Mss*. In the first case, of course, the *Mss*, and the pentlandite that subsequently exsolved from it,

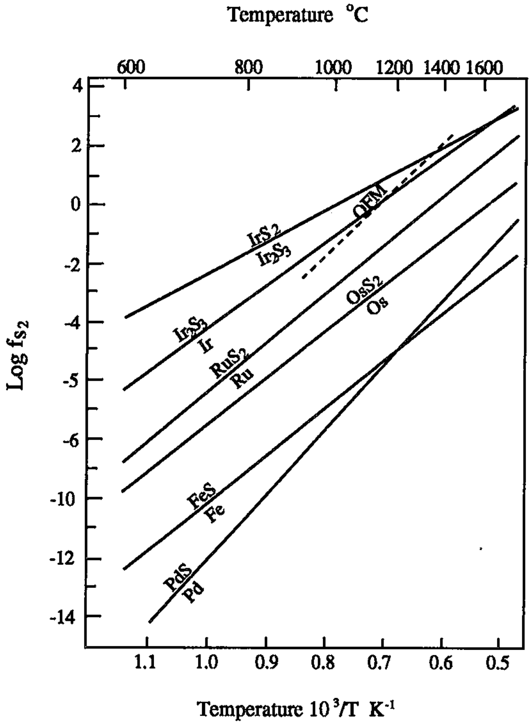

FIG. 5. Phase relationships showing Ir, Ru, Os, Pd, and Fe as a function of sulfur fugacity and temperature (from Keays *et al.* 1981). Dashed line marks the oxygen fugacity along the quartz – fayalite – magnetite buffer (from Barnes *et al.* 1988).

would be relatively depleted in Ir, but not Ru and Os, and the Ir would remain with the sulfide liquid to crystallize as discrete PGM at a later stage in the evolution. We should stress that our data on the Ir content of pyrrhotite are very limited, and that a larger data-base on Jinchuan and other deposits is required before ideas about the partitioning of Ir can be evaluated.

CONCLUSIONS

1. AMS analyses are capable of determining PGE in sulfide minerals with large grain-size (>0.3–0.4 mm) down to ppb and sub-ppb levels. This approach has great advantages over other instruments, such as the electron microprobe and the ion microprobe, particularly for examining the distribution of PGE in sulfides from PGE-poor sulfide deposits.
2. Pentlandite is the most important carrier of PGE among the major sulfide minerals in the Jinchuan Ni–Cu deposit. It can account for about 70 wt.% of the Pd, and up to 46 wt.% of the Ru, Os and Rh of the sulfide ores. The preference of Pd, Ru, Os and Rh in sulfides is pentlandite > pyrrhotite > chalcopyrite.
3. Platinum, Ir and Au are depleted in sulfide minerals; Pt and Au appear to have favored the sulfide liquid over *Mss*. The distribution of Ir may be due to later metamorphic redistribution or a function of the prevailing $f(S_2)$.
4. Palladium occurs as a dispersed component in solid solution in pentlandite; it has not reached saturation even at the highest content of 6.3 ppm in the Jinchuan pentlandite. Solid-state diffusion appears to have maintained equilibrium between *Mss* and pentlandite exsolving from it, in terms of distribution of Pd.
5. Some of the Os, Ru and Rh that have been detected in pentlandite and pyrrhotite may exist as tiny inclusions of PGM, which are the result of exsolution of the PGE from these minerals during metamorphism.

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REFERENCES

AGIORGITIS, G. & WOLF, R. (1978): Aspects of osmium, ruthenium and iridium contents in some Greek chromites. *Chem. Geol.* **23**, 267-272.

BARNES, S.J., GOLE, M.J. & HILL, R.E.T. (1988): The Agnew nickel deposit, Western Australia. II. Sulfide geochemistry, with emphasis on the platinum-group elements. *Econ. Geol.* **83**, 537-550.

_____ & NALDRETT, A.J. (1985): Geochemistry of the J-M (Howland) Reef of the Stillwater complex, Minneapolis Adit area. I. Sulfide chemistry and sulfide–olivine equilibrium. *Econ. Geol.* **80**, 627-645.

BRÜGMANN, G.E., ARNDT, N.T., HOFMANN, A.W. & TOBSCHALL, H.J. (1987): Noble metal abundances in komatiite suites from Alexo, Ontario, and Gorgona Island, Colombia. *Geochim. Cosmochim. Acta* **51**, 2159-2169.

CABRI, L.J., BLANK, H., EL GORESY, A., LAFLAMME, J.H.G., NOBILING, R., SIZGORIC, M.B. & TRAXEL, K. (1984): Quantitative trace-element analyses of sulfides from Sudbury and Stillwater by proton microprobe. *Can. Mineral.* **22**, 521-542.

_____ & LAFLAMME, J.H.G. (1976): The mineralogy of the platinum group elements from some copper–nickel deposits of the Sudbury area, Ontario. *Econ. Geol.* **71**, 1159-1195.

_____ & _____ (1981): Analyses of minerals containing platinum-group elements. *In* Platinum-Group Elements: Mineralogy, Geology, Recovery (L.J. Cabri, ed.). *Can. Inst. Mining Metall., Spec. Vol.* **23**, 151-173.

CHAI, GANG & NALDRETT, A.J. (1990): Ni–Cu–PGE mineralization of the Jinchuan Ni–Cu deposit, NW China. *Int. Mineral. Assoc., 15th Gen. Meet. (Beijing)* (abstr.)

_____ & _____ (1992): Petrology and geochemistry of the Jinchuan ultramafic intrusion: cumulate of a high-Mg basaltic magma. *J. Petrol.* **33**, 277-303.

CHRYSSOULIS, S.L., CABRI, L.J. & LENNARD, W. (1989): Calibration of the ion microprobe for quantitative trace precious metal analyses of ore minerals. *Econ. Geol.* **84**, 1684-1689.

CRAIG, J.R. & SCOTT, S.D. (1974): Sulfide phase equilibria. *In* Sulfide Mineralogy (P.H. Ribbe, ed.). *Mineral. Soc. Am., Short Course Notes* **1**, CS1-110.

CROCKET, J.H. (1981): Geochemistry of the platinum-group elements. *In* Platinum-Group Elements: Mineralogy, Geology, Recovery (L.J. Cabri, ed.). *Can. Inst. Mining Metall., Spec. Vol.* **23**, 47-64.

_____, TERUTA, Y. & GARTH, J. (1976): The relative importance of sulfides, spinels and platinoid minerals as carriers of Pt, Pd, Ir and Au in the Merensky Reef at Western Platinum Limited, near Marikana, South Africa. *Econ. Geol.* **71**, 1308-1323.

GENKIN, A.D., DISTLER, V.V., LAPUTINA, I.P. & FILIMONOVA, A.A. (1973): Geochemistry of palladium in copper–nickel ores. *Geochem. Int.* **10**, 1007-1013.

HILLENKAMP, F., UNSOLD, E., KAUFMANN, R. & NITSCHE, R. (1975): A high-sensitivity laser microprobe mass analyzer. *Appl. Phys.* **8**, 341-348.

HOFFMAN, E.L., NALDRETT, A.J., VAN LOON, J.C., HANCOCK, R.G.V. & MANSON, A. (1978): The determination of all the platinum group elements and gold in rocks and ore by neutron activation analysis after preconcentration by a nickel sulfide fire assay technique on large samples. *Anal. Chim. Acta* **102**, 157-166.

KEAYS, R.R., ROSS, J.R. & WOOLRICH, P. (1981): Precious metals in volcanic peridotite-associated nickel sulfide deposits in western Australia. II. Distribution within the ores and host rocks at Kambalda. *Econ. Geol.* **76**, 1645-1674.

KILIUS, L.R., BABA, N., GARWAN, M.A., LITHERLAND, A.E., NADEAU, M.J., RUCKLIDGE, J.C., WILSON, G.C. & ZHAO, XIAO LEI (1990): AMS of heavy ions with small accelerators. *Nucl. Instrum. Meth. Phys. Res.* **B52**, 357-365.

KULLERUD, G. (1967): Sulfide studies. *In* Researches in Geochemistry 2 (P.H. Abelson, ed.). John Wiley & Sons, New York (286-321).

LI, CHUSI, NALDRETT, A.J., RUCKLIDGE, J.C. & KILIUS, L.R. (1993): Concentrations of platinum-group elements and gold in sulfides from the Strathcona deposit, Sudbury, Ontario. *Can. Mineral.* **31**, *(in press).*

LIEBL, H. (1975): Ion probe microanalysis. *J. Phys.* **E8**, 797-808.

MAKOVICKY, M., MAKOVICKY, E. & ROSE-HANSEN, J. (1986): Experimental studies on the solubility and distribution of platinum group elements in base-metal sulfides in platinum deposits. *In* Metallogeny of Basic and Ultrabasic Rocks (M.J. Gallagher, R.A. Ixer, C.R. Neary & H.M. Prichard, eds.). Inst. Mining Metall., London (415-425).

MCLAREN, C.H. & DE VILLIERS, J.P.R. (1982): The platinum-group chemistry and mineralogy of the UG–2 chromitite layer of the Bushveld Complex. *Econ. Geol.* **77**, 1348-1366.

NALDRETT, A.J. (1966): Partial pressure of sulfur in the vapour co-existing with the $Fe_{1-x}Ni_{1-x}S$ solid solution at 600°C. *Carnegie Inst. Washington, Year Book* **65**, 326-328.

______ (1981): Nickel sulfide deposits: classification, composition and genesis. *Econ. Geol. Seventy-fifth Anniv. Vol.*, 628-685.

______, ASIF, M., GORBACHEV, N.S., KUNILOV, V.E., FEDORENKO, V.A. & LIGHTFOOT, P.C. (1992): The composition of the Ni–Cu ores of the Noril'sk region. *Can. Mineral.* **30**, 494-495 (abstr.).

OSHIN, I.O. & CROCKET, J.H. (1981): Noble metals in Thetford Mines ophiolites, Quebec, Canada. I. Distribution of gold, iridium, platinum and palladium in the ultramafic and gabbroic rocks. *Econ. Geol.* **77**, 1556-1570.

PAGE, N.J & TALKINGTON, R.W. (1984): Palladium, platinum, rhodium and iridium in peridotites and chromitites from ophiolite complexes in Newfoundland. *Can. Mineral.* **22**, 137-149.

RUCKLIDGE, J.C., GORTON, M.P., WILSON, G.C., KILIUS, L.R., LITHERLAND, A.E., ELMORE, D. & GOVE, H.E. (1982): Measurement of Pt and Ir at sub-ppb levels using Tandem-accelerator mass spectrometry. *Can. Mineral.* **20**, 111-119.

________, WILSON, G.C. & KILIUS, L.R. (1990): In situ trace element determinations by AMS. *Symp. Fifth Int. Conf. on Accelerator Mass Spectrometry, Paris* (abstr.).

S.G.U. (The Sixth Geological Unit of Gansu Geological Survey, China) (1984): *Geology of Baijiazuezhi Cu–Ni deposit.* Geological Publication Bureau, Beijing, China (in Chinese).

SHIMA, H. & NALDRETT, A.J. (1975): Solubility of sulfur in an ultramafic melt and the relevance of the system Fe–S–O. *Econ. Geol.* **70**, 960-967.

SUN, SHEN SU (1986): The discovery of Pt enrichment parts and existing status of Pt and Pd in mining area of Jinchuan sulfide Ni–Cu deposit. *Geology and Prospecting* **12**, 36-39 (in Chinese).

SWEENY, J.M. & EDGAR, A.D. (1988): The geochemistry, origin, and economic potential of platinum group element-bearing rocks of the Lac des Iles complex, northwestern Ontario. *In* Ont. Geol. Surv., Geosci. Res. Grant Program, Summary of Research 1987-1988 (V.G. Milne, ed.). *Ont. Geol. Surv., Misc. Pap.* **140**, 68-77.

VERMAAK, C.F. & HENDRIKS, L.P. (1976): A review of the mineralogy of the Merensky Reef, with specific reference to new data on the precious metal mineralogy. *Econ. Geol.* **71**, 1244-1269.

WILSON, G.C., KILIUS, L.R. & RUCKLIDGE, J.C. (1991): *In situ* analysis of precious metals in polished mineral samples and sulfide "standards" by accelerator mass spectrometry at concentrations of parts-per-billion. *Geochim. Cosmochim. Acta* **55**, 2241-2251.

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