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CONCENTRATIONS OF PLATINUM-GROUP ELEMENTS AND GOLD IN SULFIDES FROM THE STRATHCONA DEPOSIT, SUDBURY, ONTARIO

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ABSTRACT

Sulfide minerals and magnetite from the Strathcona deposit, Sudbury, Ontario, have been analyzed for the platinum-group elements (PGE) and Au with *in situ*, ultra-sensitive accelerator mass spectrometry (AMS). Pyrrhotite contains Ir, Rh and Ru at levels close to those of the bulk sulfide ores (recalculated to 100% sulfides), ranging from tens to more than 100 ppb; Pt, Pd and Au are present in the pyrrhotite at much lower levels than in the bulk sulfide ores. Among all the other minerals, including pentlandite, chalcopyrite, cubanite, bornite and magnetite, pentlandite is the only phase that accommodates significant amounts of Pd, with concentrations in the range from hundreds to thousands of ppb. The concentrations of the other PGE and Au are extremely low in all of the sulfides and magnetite in comparison with the values of the ores. They range from several ppb to sub-ppb levels. Although pentlandite contains significant amounts of Pd, its overall contribution to the ore of the Deep Copper Zone is not great because the ore contains only small amounts of this mineral. Mass-balance calculations indicate that most of the Pt, Pd and Au in the ore is not present in the sulfides and magnetite, but must occur in discrete accessory minerals. The partition coefficients of PGE between *Mss* and sulfide liquid have been estimated from the compositions of minerals and ore to be 6.5×10^{-3} to 8.6 10^{-2} for Pt, 6.8×10^{-3} to 3.9×10^{-2} for Pd, 4.7×10^{-3} to 8.0×10^{-2} for Au, and 5.9 to 6.7 for Ir. The variations in the concentrations of Pt and Ir in the deposit can be explained by a process involving fractional crystallization of monosulfide solid solution (*Mss*) from a parental sulfide liquid and mixing of varying proportions of variably fractionated liquid with *Mss*, if the partition coefficients between *Mss* and sulfide liquid are less than 0.1 for Pt and from 6.7 to 3.5 for Ir.

Keywords: platinum-group elements, partition coefficient, fractionation, sulfides, accelerator mass spectrometry, Strathcona deposit, Sudbury, Ontario.

SOMMAIRE

Nous avons analysé les sulfures et la magnétite provenant du gisement de Strathcona, à Sudbury, en Ontario, pour les éléments du groupe du platine et pour l'or par spectrométrie de masse avec accélérateur, méthode *in situ* ultra sensible. La pyrrhotite contient Ir, Rh et Ru à des niveaux semblables à ceux dans les échantillons de minerai (recalculés sur une base de 100% sulfures), dans l'intervalle de dizaines à plus de 100 ppb. Par contre, Pt, Pd et Au sont présents dans la pyrrhotite à des niveaux beaucoup plus faibles que dans le minerai global. De tous les autres minéraux, y compris pentlandite, chalcopyrite, cubanite, bornite et magnétite, seule la pentlandite peut accommoder des concentrations appréciables de Pd, dans l'intervalle de centaines à des milliers de ppb. La concentration des autres minéraux du groupe du platine et de l'or est extrêmement faible dans tous les sulfures et la magnétite en comparaison des valeurs pour les échantillons de minerai, de quelques ppb à des niveaux inférieurs au ppb. Quoique la pentlandite contienne des concentrations importantes de Pd, sa contribution à la constitution du minerai dans la zone dite "Deep Copper" n'est pas importante. Des calculs du bilan des masses montrent que la plupart du Pt, du Pd et de l'Au dans le minerai se trouverait non dans les sulfures ni la magnétite, mais plutôt sous forme de minéraux accessoires distincts. Le coefficient de partage des éléments du groupe du platine entre solution solide monosulfurée et liquide sulfuré a été estimé à partir de la composition des minéraux et du minerai: entre 6.5×10^{-3} et 8.6×10^{-2} pour le Pt, entre 6.8×10^{-3} et 3.9×10^{-2} pour le Pd, entre 4.7×10^{-3} et 8.0×10^{-2} pour l'Au, et entre 5.9 et 6.7 pour l'Ir. Les variations dans la concentration de Pt et de Ir dans le gisement s'expliquent par un processus impliquant cristallisation fractionnée d'une solution solide monosulfurée à partir d'un liquide sulfuré parent, et mélange en proportions variables d'un liquide variablement évolué et du monosulfure, si les coefficients de partage entre monosulfure et liquide sulfuré sont inférieurs à 0.1 pour le Pt, et entre 6.7 et 3.5 pour l'Ir.

(Traduit par la Rédaction)

Mots-clés: éléments du groupe du platine, coefficient de partage, fractionnement, sulfures, spectrométrie de masse avec accélérateur, gisement de Strathcona, Sudbury, Ontario.

INTRODUCTION

Knowledge of the distribution of platinum-group elements (PGE) in sulfide minerals is important not only for mineral processing, but also for a full understanding of the fractionation of these elements during the crystallization of a sulfide liquid. Previous attempts to establish whether the PGE, other than those occurring as discrete platinum-group minerals (PGM), also occur as dilute solid-solutions in the minerals from the Sudbury ores, were made with the electron microprobe (Cabri & Laflamme 1976) and proton microprobe (Cabri *et al.* 1984). Pt, Pd or Rh were not detected in chalcopyrite, pentlandite and pyrrhotite because the analyses were limited by detection limits in the ranges 300–500 ppm (electron microprobe) and 1–60 ppm (proton microprobe). Recently, *in situ* analysis of sulfides for heavy elements by accelerator mass spectrometry (AMS) at the IsoTrace Laboratory, University of Toronto, has been developed to the point at which samples can be routinely analyzed for the PGE and Au at the ppb and sub-ppb levels (Wilson *et al.* 1991). This technique has been used as a complementary tool to the electron and proton microprobes in the measurement of concentrations of PGE and Au in sulfide minerals from Sudbury (Li & Naldrett 1990). As a follow-up to the initial AMS study, base-metal sulfide minerals from different ore-zones of the Strathcona deposit at Sudbury were analyzed. The selected samples of ores also were analyzed for whole-rock PGE and Au using the technique of neutron activation combined with fire-assay preconcentration. The distribution of PGE and Au in individual minerals and its significance to the metal zonation in the deposit form the main subject of this paper.

ANALYTICAL TECHNIQUES

Accelerator mass spectrometry

Specimens used in this analysis are polished mineral surfaces. The preparation technique has been described by Wilson *et al.* (1991). Inclusion-free areas of coarse-grained crystals selected with an optical microscope were further examined by scanning electron microprobe to assess the presence of very small inclusions of PGM. Selected targets were then drilled out under water with a hollow, diamond-edged core drill of 4 mm internal diameter at a speed of 4750 rpm. The cylindrical "minicores" were washed and dried in air. A set of 12 such cores, including standards of pure copper and SARM–7 in a sulfide bead, were loaded into the sample chamber of the accelerator mass spectrometer and aligned optically prior to bombarding with a 30 keV Cs^+ primary ion beam. Negative secondary ions were sputtered, ionized in or near the target grains, and extracted from the sample chamber at 20 keV. Electric and magnetic filtering of the ions, followed by acceleration to 2 MeV and change in charge from negative to positive, results in the elimination of all molecules whose mass could match that of the selected isotope. This procedure reduces the background to vanishingly small levels, and thus gives extraordinarily good sensitivities for the trace elements being studied. The light group of isotopes, ^{106}Pd, ^{103}Rh and ^{101}Ru, were analyzed in the 5+ charge state, energy 12 MeV, whereas the heavier group, ^{197}Au, ^{196}Pt, ^{193}Ir and ^{188}Os, were analyzed in the 6+ charge state, energy 14 MeV. Mean count rates were converted to element concentrations with reference to the sulfide bead of the SARM–7 standard.

The detection limits, quoted on the basis of equal counting times of 100 seconds, are down to Au 0.003 ppb, Pt 0.18 ppb, Rh 0.57 ppb, Ir 0.6 ppb, Pd 2.1 ppb, Ru 4.6 ppb, and Os 48 ppb.

Neutron-activation analysis

PGE and Au were determined with a fire-assay and neutron-activation technique modified after that of Hoffman *et al.* (1978). Cu-rich ore samples were reduced to 10 grams, and additional Ni was added to achieve a ratio Ni/Cu greater than 3 in the fire-assay bead. The content of sulfur in the mixture was calculated to achieve the stoichiometric ratio of NiS and Cu_2S. The sulfide beads were then dissolved in hydrochloric acid, and the residues were collected in plastic bags for irradiation. Samples were irradiated for three minutes at the Nuclear Reactor Center of McMaster University, and then counted three minutes for Pd and Rh after a decay of three minutes. For the other elements, samples were irradiated for one hour and then counted about 1.5 hours after one week decay in the Department of Geology, University of Toronto. Samples with low levels of Os, Ir and Ru (<0.2 ppb) were counted anew for Os, Ir and Ru after approximately four weeks of decay. The detection limits (three sigma times the square root of the background) are down to Ir 0.01, Au 0.02, Rh 0.5, Os 1.0, Ru 3, Pd 3 and Pt 5 ppb.

GEOLOGICAL BACKGROUND AND SAMPLES SELECTED

The Strathcona deposit is located on the North Range of Sudbury Igneous Complex (SIC) (Fig. 1). The ore lies at the basal contact of the complex and in the footwall (Fig. 2). The geology of this deposit has been described by Naldrett & Kullerud (1967), Cowan (1968), Abel *et al.* (1979), Abel (1981), Coats & Snajdr (1984) and Li *et al.* (1992). Four types of ore are observed. Disseminated sulfides of the Hangingwall Zone occur within the Sublayer norite. This zone is underlain by the Main Zone, which consists of massive and disseminated ore within the Footwall breccia. The Deep Zone consists of stringers of massive sulfides that were emplaced in fractures within the footwall gneiss. Pyrrhotite, chalcopyrite, magnetite and pyrite are the major minerals in each of the preceding ore-zones. Copper-rich stringers containing chalcopyrite and cubanite (Copper and Deep

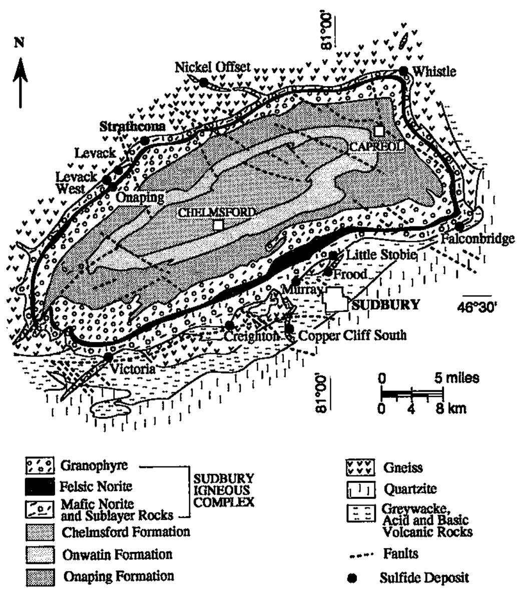

FIG. 1. Geological map of the Sudbury region (after Pye *et al.* 1984).

Copper Zones), with minor magnetite, pentlandite, pyrrhotite and sphalerite, occur 100–500 meters into the footwall.

The Strathcona deposit has been interpreted as a typical magmatic sulfide deposit by many investigators (Naldrett & Kullerud 1967, Cowan 1968, Keays & Crocket 1970, Chyi & Crocket 1976, Abel *et al.* 1979, Naldrett *et al.* 1982). Farrow & Watkinson (1992), however, suggested that the sulfide veins of the Deep Copper Zone are of hydrothermal origin because of the occurrence of hydrous alteration associated with the ores. Li *et al.* (1992) proposed that the Deep Copper Zone is the end-product of the fractionation of an original sulfide magma giving rise to the entire deposit, because the composition of the Deep Copper Zone follows the trend of the compositional variations in the deposit. They argued that the thin alteration-induced selvages along the sulfide veins represent typical contact alterations resulting from the emplacement of a sulfide liquid in the footwall.

Most samples in this study were collected from the Deep Copper Zone. Chalcopyrite is the most abundant sulfide mineral in this zone. It occurs as mosaic patches that usually enclose other sulfide and oxide minerals. Coarse grains are up to 3 mm across. Cubanite is the next most abundant sulfide mineral. It occurs as coarse laths up to 0.5 mm across in chalcopyrite or as massive round patches together with chalcopyrite. Pyrrhotite and pentlandite constitute only a small proportion of the sulfides. Pyrrhotite occurs invariably as small inclusions in chalcopyrite or cubanite. Pentlandite is present as massive blocky crystals up to 5 cm across. Bornite and millerite are minor sulfides. Millerite is present as coarse grains together with quartz, usually at the termination of veins. Magnetite occurs throughout the sulfide assemblage as anhedral to euhedral grains up to several mm in diameter.

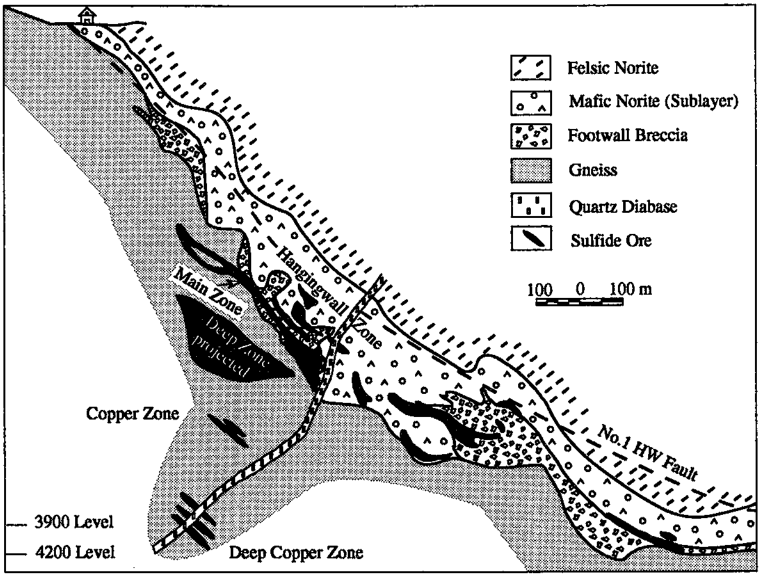

FIG. 2. Vertical cross-section through the Strathcona deposit (6280 E, looking East).

Additional samples were collected from the Hangingwall Zone for the analysis of pyrrhotite. The blocky, coarse-grained pyrrhotite, together with pentlandite, magnetite, chalcopyrite and pyrite, are interstitial to silicates within the Sublayer norite.

RESULTS

The concentrations of PGE and Au in the ore samples are given in Table 1, and their concentrations in 100% sulfides are listed in Table 2. The samples selected from the Deep Copper Zone for the AMS single-crystal analysis are enriched in one particular mineral. Those samples enriched in accessory minerals such as millerite (R–3, R–6B, L–18, L–23 and P–4) and bornite (898–3) have unusual compositions with respect to the typical massive ores of the Deep Copper Zone (Table 2). The average concentrations of PGE and Au in the sulfide fraction of the Deep Copper Zone given by Li *et al.* (1992) are used in the following discussion where the composition of the zone is concerned.

The concentrations of PGE and Au in minerals are listed in Table 3. The values in parentheses in Table 3 express the ranges of four analyses. They vary from less than 10% up to 70% of the means. The variations are primarily attributed to the inhomogeneous distribution of the PGE in a single grain.

Pyrrhotite

Au and all of the PGE except Os were detected in pyrrhotite. The concentration of Os in most grains of pyrrhotite is below the detection limit; only one grain was found to contain measurable Os at 52 ppb, slightly higher than the detection limit. Three grains were analyzed in each of two samples (H90–9 and H90–10). The variations of the PGE among different grains range from 4% up to more than 50%, indicating inhomogeneous distribution of these elements in different grains. When compared with the concentrations of these elements in the bulk sulfide ore, Pt, Pd and Au in pyrrhotite are very much lower, whereas Os, Ir, Rh and Ru in pyrrhotite are close to the levels in the bulk ore.

TABLE 1. CONCENTRATIONS OF PGE AND BASE METALS IN THE ORES OF THE STRATHCONA DEPOSIT

Sample	Os	Ir	Ru	Rh	Pt	Pd	Au	Ni	Cu	S
Hangingwall Zone										
H90-8	15.4	37	39.9	58	45	14	5	1.98	0.12	18.1
H90-9	17.4	40	47.3	43	32	23	3	1.57	0.08	15.7
H90-10	32.3	66	74.5	96	33	12	3	2.97	0.04	27.3
Deep Copper Zone										
R-3	<1	0.08	<3	<0.5	710	8952	33	49.00	0.16	30.8
R-4	<1	<0.01	<3	<0.5	2670	740	151	0.42	36.00	32.0
R-6B	<1	0.04	<3	<0.5	1109	12904	7	40.40	0.62	31.5
R-10	<1	0.11	<3	<0.5	5607	9214	159	1.06	32.50	30.3
R-15	<1	0.10	<3	<0.5	1260	468	7	0.82	26.80	33.0
L-18	<1	0.04	<3	<0.5	6339	6022	3151	6.85	1.86	5.4
L-23	<1	<0.01	<3	<0.5	11154	3364	909	30.90	1.45	19.0
898-3	<1	0.35	<3	<0.5	1574	—	117	0.43	43.60	20.4
898-5	<1	0.21	<3	<0.5	476	2301	24	28.10	1.92	26.6
898-6	<1	0.27	<3	<0.5	7718	3428	14874	1.21	20.40	18.6
P-4	<1	0.49	<3	<0.5	822	245	1236	47.60	2.86	27.3
MT-1	<1	0.30	<3	<0.5	8054	6376	629	5.37	19.30	25.7

Note: PGE and Au are in ppb, Ni, Cu and S are in wt percent. —: not determined.

TABLE 2. CONCENTRATIONS OF METALS[1] IN THE BULK ORES (100% SULFIDES) OF THE STRATHCONA DEPOSIT

Sample	Os	Ir	Ru	Rh	Pt	Pd	Au	Cu	Ni	S
Hangingwall Zone										
H90-8	34	80	87	125	97	30	11	0.27	4.3	39.96
H90-9	43	100	119	108	79	56	8	0.32	3.9	38.79
H90-10	46	94	107	136	47	16	4	0.26	4.2	38.88
Average	39	91	104	123	74	34	8	0.28	4.1	39.21
Deep Copper Zone[2]		0.11			4719	5213	296	26.21	2.2	32.40

[1] PGE and Au are in ppb, Cu, Ni and S are in wt percent.

[2] The concentrations of PGE are the average values of 32 typical massive sulfide ores given by Li *et al.* (1992), the concentrations of Ni, Cu and S are the average values of 1577 massive sulfide ores analyzed by Falconbridge Ltd.

Pentlandite

As in pyrrhotite, inhomogeneous distribution of PGE in different grains are also present in the samples of pentlandite from the Deep Copper Zone. Pentlandite contains significant amounts of Pd, ranging from 331 to 2088 ppb. These values, however, are less than one half of the values of the bulk sulfide ore. Ru was not detected in any of the grains. Os and Rh are above the detection limits in only one grain. Half of the samples have Ir higher than the detection limits. Except for Pd, all the other elements in pentlandite are very much lower than their levels in the bulk ore.

Chalcopyrite, cubanite, millerite, bornite and magnetite

No significant amounts of PGE or Au have been measured in any of those minerals from the Deep Copper Zone. Ru, Rh, Ir and Os in all of the samples are lower than the detection limits. Levels of Pd in these minerals are in the range 4 to 41 ppb. Pt ranges from less than 0.18 to 5.6 ppb, and Au, from 0.07 to 58 ppb. These values are much lower than those of the bulk sulfide ore, for which typical values are 4719 ppb Pt, 5213 ppb Pd and 296 ppb Au.

DISCUSSION

Distribution of the PGE in the Hangingwall Zone

Assuming that pyrrhotite, pentlandite and chalcopyrite are the only sulfide minerals present, we have then used the concentrations of Ni, Cu and S in the bulk ore to calculate the concentrations of these minerals in the Hangingwall Zone. The proportions of pyrrhotite, pentlandite and chalcopyrite in the Hangingwall Zone

TABLE 3. CONCENTRATIONS OF PGE AND Au IN SULFIDES AND MAGNETITE FROM THE STRATHCONA DEPOSIT

Mineral	Sample	Pt	Au	Ir	Os	Pd	Rh	Ru
Po	H90-8	9.0 (5.1)	0.14 (0.03)	81 (8)	nd	6.8 (1.7)	109 (3)	206 (19)
	H90-9	6.0 (1.4)	0.15 (0.01)	61 (8)	nd	4.8 (1.8)	54 (3)	114 (3)
		8.3 (2.8)	0.2 (0.05)	53 (8)	nd	7.3 (4.0)	53 (10)	154 (12)
	Average	7.2 (1.6)	0.18 (0.04)	57 (6)	nd	6.1 (1.8)	53.5 (0.5)	134 (28)
	H90-10	0.6 (0.16)	0.15 (0.03)	105 (4)	52 (21)	3.7 (1.1)	171 (5)	114 (26)
		nd	0.27 (0.08)	95 (17)	nd	5.7 (2.6)	138 (3)	154 (26)
		0.4 (0.06)	2.86 (1.34)	99 (4)	nd	5.9 (3.2)	58 (14)	170 (19)
	Average	< 0.5	1.1 (1.5)	100 (5)	< 52	5.1 (1.2)	122 (58)	146 (29)
Average (Po)		< 5.6	0.47 (0.54)	79 (22)	< 52	6.0 (0.9)	95 (36)	162 (39)
Pn	898-5	0.54 (0.58)	3.1 (0.6)	nd	nd	311 (122)	nd	nd
	R-3	3.1 (0.9)	2 (0.3)	nd	nd	1502 (270)	nd	nd
	R-6B	0.7 (0.04)	1.2 (0.01)	nd	nd	2088 (167)	nd	nd
		2.2 (1.0)	1.3 (0.9)	nd	nd	1126 (799)	nd	nd
		1.5 (0.14)	1.3 (0.15)	nd	nd	771 (345)	0.6 (0.4)	nd
Average (Pn)		1.61 (1.1)	1.78 (0.8)	nd	nd	1170 (680)	<0.6	nd
Mil	L-18	0.86 (0.23)	0.1 (0.02)	0.9 (0.5)	nd	36 (9)	nd	nd
	L-23	0.9 (0.2)	58 (12)	nd	nd	20 (8)	nd	nd
	P-4	0.16 (0.02)	7.21	nd	nd	9	nd	nd
		1.2 (0.3)	6.0 (0.6)	nd	nd	15 (5)	0.7 (0.2)	nd
Average (Mil)		0.78 (0.4)	17.8 (27)	<0.9	nd	20 (12)	<0.7	nd
Ccp	898-6	4.1 (0.6)	14.8 (1.9)	nd	nd	41 (12)	nd	nd
	R-4	5.6 (0.3)	15 (0.4)	5.8 (1.5)	nd	28 (5)	0.7 (0.2)	nd
	R-10	1.2 (0.2)	3 (0.2)	nd	nd	27 (5)	nd	nd
	R-15	1.14 (0.08)	0.3 (0.02)	nd	nd	5 (2)	0.6 (0.3)	nd
		0.46 (0.26)	0.72 (0.21)	1.4 (0.3)	nd	23 (4)	nd	nd
Average (Ccp)		2.5 (2.2)	6.8 (7.5)	<3.6	nd	25 (13)	<0.65	nd
Cub	R-15	0.25 (0.05)	0.46 (0.08)	nd	nd	20 (10)	nd	nd
Mag	MT-1	nd	0.07 (0.02)	nd	nd	4 (3)	nd	nd
Bn	898-3	1.24 (0.06)	0.09	nd				
MDL*		0.18	0.003	0.6	48	2.1	0.57	4.6

All elements in ppb. (+/-): ranges of concentration; MDL: detection limit; nd: not detected. Po: pyrrhotite Ccp: chalcopyrite; Pn: pentlandite; Cub: cubanite; Bn: bornite; Mil: millerite; Mag: magnetite.

have been estimated to be 88.4, 10.8 and 0.8 wt. %, respectively. Using average values for both pyrrhotite and for the bulk sulfide ore, a mass-balance calculation indicates that 100% of the Ru, 77% of the Ir, and 68% of the Rh occur in pyrrhotite. Only 7% of the Pt, 16% of the Pd and 5% of the Au in bulk ore can be accounted for by pyrrhotite. Because the samples are apparently free of discrete micrograins of PGM at the resolution of an SEM analysis, it is likely that these PGE in pyrrhotite occur either in solid solution or as submicrometer-size exsolved particles similar to the particles and atomic clusters of gold described as occurring in pyrite by Bakken *et al.* (1989). Only small amounts of Pt, Pd and Au occur in the pyrrhotite. The majority of the Pt and Au in the bulk ore must occur as discrete precious minerals or in other phases. No detailed mineralogical investigation has been carried out in this zone. Data from two neighboring deposits, the Levack West and Coleman, indicate that Pt occurs as moncheite ($PtTe_2$), insizwaite ($PtBi_2$) and niggliite (PtSn) (Cabri & Laflamme 1976). It is likely that Pt in the Hangingwall Zone at Strathcona also occurs primarily as these phases.

PGE distribution in the Deep Copper Zone

Ir, Os, Rh and Ru in both the sulfide minerals and the bulk ores in the Deep Copper Zone were not detected by either AMS or neutron-activation analysis. Among the other elements, only Pd is detected at significant levels in pentlandite. Concentrations of Pt and Au in all the minerals are extremely low in comparison with their concentrations in the bulk sulfide ore. The composition of the Deep Copper Zone, calculated from results of 1577 analyses of massive ore (analyzed by Falconbridge

Ltd.), is 26.21% Cu, 2.17% Ni and 32.35% S. If all the Ni occurs as pentlandite, this amounts to 5.7 wt.% pentlandite. This is a maximum value because the ore also contains minor amounts of another Ni-bearing mineral, millerite. Although pentlandite accommodates appreciable amounts of Pd, its contribution to the bulk ore is not great because of its low concentration. A mass-balance calculation indicates that only 1.3% of the Pd of the ore occurs in pentlandite. More than 98% of the Pd, as well as almost 100% of the Pt and Au, must occur in other phases. A detailed mineralogical investigation has shown that much of the Pt and Pd occur as discrete minerals involving Te, Bi, Sn and As in microfractures and along grain boundaries of sulfide minerals in the Deep Copper Zone (Li & Naldrett 1993).

Partitioning of PGE between Mss and sulfide liquid

If we accept the fractional crystallization model for the gross zoning of the Strathcona deposit (Naldrett *et al.* 1982, Li *et al.* 1992), we can calculate the composition of the parental sulfide liquid giving rise to the deposit from the ore reserves and compositions of the different ore zones in the deposit. The results of the calculations are given in Table 4.

The partitioning of PGE between monosulfide solid solution (*Mss*) and sulfide liquid can be estimated in two ways. First, let us consider Pt. If the present Pt content of the pyrrhotite in the Hangingwall Zone (5.6 ppb) were that of the original *Mss* crystallizing from the parental sulfide liquid, the partition coefficient would have been 6.5×10^{-3}. However, the experimental data of Makovicky *et al.* (1986) have shown that a considerable amount of PGE can enter into the *Mss* at high temperature and exsolve at lower temperature. The present content of Pt in pyrrhotite may not represent the concentration in *Mss* at the time of its crystallization but may well be low. Therefore, the partition coefficient is a minimum value.

If, on the other hand, the present Pt content of the Hangingwall Zone is taken to be that of the original *Mss* (74 ppb), the partition coefficient would be 8.6×10^{-2}. This supposition also represents a simplification, since the sulfides of the Hangingwall Zone are likely to have started as a mixture of original *Mss* and trapped sulfide liquid. Since the partition coefficient is less than one in either case, the trapped sulfide liquid would have contained more Pt than the *Mss*, so that the Pt content of the *Mss* obtained in this second way is a maximum, and so is the partition coefficient. Thus the actual value of the coefficient, D_{Pt} (the concentration of Pt in *Mss* divided by the concentration of Pt in the liquid), is between 8.6×10^{-2} and 6.5×10^{-3}. The former seems to agree with the experimentally determined partition coefficient from the system Fe–Cu–Pt–S at 900°C, from 0.2 to 8×10^{-2} (Makovicky *et al.* 1986).

Application of a similar reasoning to Pd, Au and Ir leads to the partition coefficients listed in Table 5. The partition coefficients of Pd and Au are similar to that of Pt. The value of D_{Ir} is more than 5.

Model for the origin of the ore zonation

The Hangingwall Zone has been ascribed to the result of gravitational settling of an immiscible sulfide liquid within the Sublayer norite, and its subsequent fractional crystallization to yield *Mss* cumulate and a fractionated sulfide liquid (Naldrett & Kullerud 1967, Naldrett *et al.* 1982). The ore zones in the footwall are considered to

TABLE 4. CONCENTRATIONS OF PGE IN THE STRATHCONA DEPOSIT

Ore zone	Ore reserve (tonne x 10^6)	Mass of sulfides (tonne x 10^6)	Proportion of sulfides	Elements[1] (in 100% sulfides) Ir	Pt	Pd	Au
Ni Zone[2]	31.226	14.01	90%	15	447	410	78
Copper Zone[3]	0.976	0.28	2%	0.08	3927	4800	290
Deep Copper Zone[4]	7.627	1.22	8%	0.11	4719	5213	296
Strathcona Deposit		15.51	100%	13.5	858	882	100

[1] All elements are in ppb.

[2] Ni Zone = Hangingwall Zone + Main Zone + Deep Zone; their proportions are from Cowan (1968), the concentrations of PGE in the sulfide fractions of the Main and Deep Zones are from Naldrett *et al.* (1982), and those of the Hangingwall Zone from this study; ore reserves are from C.J.A. Coats (superintendent, Falconbridge Ltd., Sudbury Operation, personal comm.).

[3] Ore reserve is from Abel (1981); the concentrations of PGE in the sulfide fraction of the ore are from Li *et al.* (1992).

[4] Ore reserve is from Falconbridge Ltd. (Intern. Rep., 1986); the concentrations of PGE in the sulfide fraction of the ore are from Li *et al.* (1992).

TABLE 5. PARTITIONING OF PGE BETWEEN Mss AND SULFIDE LIQUID

	Ir	Pt	Pd	Au
Inferred parental liquid*	13.5	858	882	100
Pyrrhotite (Po)	79	5.6	6	0.47
Hangingwall Zone (HZ)	91	74	34	8
$D^{Po/liquid}$	5.9	6.5×10^{-3}	6.8×10^{-3}	4.7×10^{-3}
$D^{HZ/liquid}$	6.7	8.6×10^{-2}	3.9×10^{-2}	8.0×10^{-2}

* All elements are in ppb (see Table 4 for calculations).

have been emplaced by injection of the residual sulfide liquid into fractures in the footwall (Naldrett *et al.* 1982, Li *et al.* 1992). The values of D_{Pt} and D_{Ir} estimated above may be used to test the hypothesis.

The composition of the Strathcona ore is such that *Mss* would be the first mineral to crystallize, according to phase relations in the system Fe–Ni–S (Kullerud *et al.* 1969). If the residual liquid was able progressively to drain down into the footwall, perfect fractional crystallization could result. Let us consider an incompatible element Pt and a compatible element Ir. Figure 3 illustrates the compositional variations of *Mss* and its coexisting liquid during this process. The parallelogram on the left is a model for a D_{Ir} of 6.7 and a D_{Pt} of 8.6×10^{-2}. The shaded parallelogram is another model, for a D_{Ir} of 3.5 and a D_{Pt} of 8.6×10^{-2}. The composition of any mixture of *Mss* and its coexisting liquid is defined by the tie-lines (F) between the coexisting phases. Notice that both axes are drawn on a logarithmic scale and that the relative distances of a composition point to the tie-lines are not proportional to their weight volumes in the mixture. For instance, point M (representing the Main Zone) in the shaded parallelogram, although it lies close to the middle of the tie-line (F = 60), actually represents a mixture of 68% *Mss* and 32% liquid. The model with higher D_{Ir} (unshaded parallelogram) accounts better for the composition of the Hangingwall Zone. The Main and Deep Zones can be interpreted as the mixtures of cumulate *Mss* with liquid. The Copper and Deep Copper Zones can be interpreted as the residual liquid after about 85% of crystallization with respect to their Pt contents, but their Ir contents are higher than the predicted values in the model. The model with the lower D_{Ir} (shaded parallelogram) can satisfy the composition of the Copper and Deep Copper Zones, but it fails to explain the concentration of Ir in the Hangingwall Zone. The problem with the content of Ir can be eliminated if D_{Ir} is greater than 3.5 at a high temperature and decreases on cooling. Available experimental data on the PGE other than Ir indicate that their solubility in *Mss* decreases with temperature (Makovicky *et al.* 1986). If the solubility of Ir in *Mss* also decreases with temperature, the value of D_{Ir} would decrease during crystallization.

In summary, if the partition coefficients between *Mss* and sulfide liquid are about 8.6×10^{-2} for D_{Pt} and from 6.7 to 3.5 for D_{Ir}, the ore zonation in the Strathcona deposit can be interpreted as the consequence of fractional crystallization of *Mss* from a sulfide liquid with respect to the concentrations of Pt and Ir of the ores.

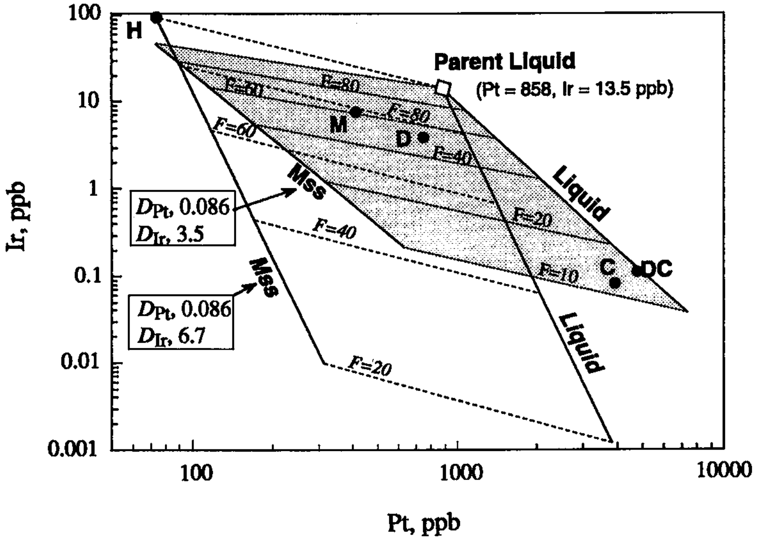

FIG. 3. Fractional crystallization of *Mss* from a sulfide liquid. Remaining liquid (F) is in wt. percent. Solid circles labeled with H, M, D, C and DC are the projections of the Hangingwall, Main, Deep, Copper and Deep Copper Zones, respectively. The compositions of the Main and Deep Zones are from Naldrett *et al.* (1982).

CONCLUSIONS

1. Most of the Ru, Rh and Ir in the Hangingwall Zone is located in pyrrhotite.

2. Pentlandite in the Deep Copper Zone contains a significant amount of Pd, but its overall contribution to the ore is not great, because only a minor amount of this mineral is present in this zone.

3. Chalcopyrite, cubanite, bornite and magnetite do not contain appreciable amounts of PGE and Au.

4. Most of Pt, Pd and Au in the Deep Copper Zone must occur as discrete grains of platinum-group minerals and gold.

5. The partition coefficients of Pt and Ir between *Mss* and sulfide liquid estimated from compositions of minerals and ore are between 8.6×10^{-2} and 4.7×10^{-3} for Pt, Pd and Au, and between 5.9 and 6.7 for Ir.

6. The variations of Pt and Ir contents in the deposit can be explained by a process involving fractional crystallization of *Mss* from a parent sulfide liquid and mixing of varying proportions of variably fractionated liquid with *Mss* if the values of D_{Pt} and D_{Ir} between *Mss* and the sulfide liquid are about 8.6×10^{-2} and less than 6.7, respectively.

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