

PLATINUM-GROUP MINERALS FROM THE DEEP COPPER ZONE OF THE STRATHCONA DEPOSIT, SUDBURY, ONTARIO

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ABSTRACT

Among the different ore zones of the Strathcona deposit, in the Sudbury district, Ontario, the Deep Copper Zone has the highest concentrations of platinum and palladium. Most of the Pt and Pd is not present in solid solution in base-metal sulfides and magnetite; rather, they occur as platinum-group minerals (PGM). These include niggliite, froodite, insizwaite, paolovite, sperrylite, michenerite, sobolevskite and a palladium chloride. The PGM, up to 50 μm across, are intergrown with tellurides (hessite and altaite), native bismuth and bismutite. They occur mainly along grain boundaries and in microfractures in sulfide minerals, magnetite, and silicates. Mass-balance calculations indicate that sperrylite and niggliite are the most abundant platinum-bearing minerals, and froodite and michenerite are the most abundant palladium-bearing minerals. Textural relationships suggest that the deposition of the PGM occurred mostly later than that of base-metal sulfides and magnetite. The occurrence of Pd chloride associated with other PGM suggests that Cl may have been an important agent for the transport and deposition of Pd. Other important elements involved in the precipitation of the PGM include Bi, Te, As and Sn.

Keywords: platinum-group elements, platinum-group minerals, Pd chloride, sulfides, Strathcona deposit, Sudbury, Ontario.

SOMMAIRE

Parmi les différentes zones minéralisées exploitées dans le gisement de Strathcona, à Sudbury, en Ontario, la zone profonde riche en Cu possède les concentrations les plus élevées en Pt et Pd. La plus grande partie de ces éléments n'existe pas sous forme de solution solide dans les sulfures des métaux de base ou dans la magnétite. Nos observations indiquent plutôt la présence de minéraux du groupe du platine, dont niggliite, froodite, insizwaite, paolovite, sperrylite, michenerite, sobolevskite et un chlorure de palladium. Ces minéraux, qui atteignent une dizaine de micromètres de diamètre, montrent une intercroissance avec des tellurures (hessite et altaite), bismuth natif et chlorure de bismuth. On les trouve surtout le long des contacts entre minéraux et dans des microfissures qui recoupent les sulfures, la magnétite et les silicates. Des calculs de proportions de minéraux montrent que sperrylite et niggliite sont les porteurs de Pt les plus importants, tandis que froodite et michenerite seraient les phases palladières les plus importantes. Les relations texturales de tous ces minéraux font penser que les minéraux du groupe du platine sont tardifs par rapport aux sulfures des métaux de base et à la magnétite. La présence d'un chlorure de Pd associé démontrerait l'importance du Cl comme agent de transfert et de déposition du Pd. D'autres éléments importants dans ce transfert seraient Bi, Te, As et Sn, d'après la composition actuelle des minéraux du groupe du platine.

(Traduit par la Rédaction)

Mots-clés: minéraux du groupe du platine, chlorure de Pd, minéralisation, éléments du groupe du platine, gisement de Strathcona, district de Sudbury, Ontario.

INTRODUCTION

Previous studies of the Strathcona deposit, Sudbury, Ontario, have shown that the distribution of the platinum-group elements (PGE) in this deposit is zoned. The concentrations of Pt, Pd, Au and Cu increase progressively from the Hangingwall Zone, within the contact of the Sudbury Igneous Complex (SIC), toward the ore zones in the footwall, whereas Rh, Ru, Ir and Os show the reverse trend (Naldrett *et al.* 1982). The Deep Copper Zone, which is located about 500 meters away from the contact into the

footwall, is marked by the highest concentrations of Pt and Pd (about 5 ppm each). Analyses of the ore minerals, including chalcopyrite, cubanite, pentlandite, millerite, bornite and magnetite, by accelerator mass spectrometry has indicated that most of Pt and Pd in the ore are not present in these minerals (Li *et al.* 1991).

This paper reports the mode of occurrence of the platinum-group minerals (PGM) in the Deep Copper Zone of the Strathcona deposit, their mutual textural relationships, as well as relationships with the sulfides and magnetite of the ores.

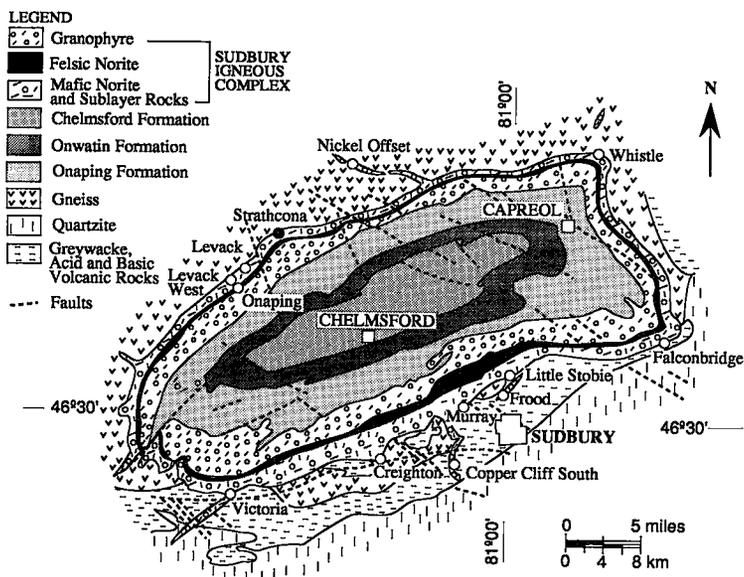


FIG. 1. Geological map of the Sudbury region (after Pye *et al.* 1984).

GEOLOGY OF THE DEEP COPPER ZONE

The Deep Copper Zone is one of the Cu-rich stringers at the Strathcona deposit, which is located on the North Range of the SIC (Fig. 1). It is the ore zone that is located farthest from the contact of the SIC (Fig. 2). The

characteristics of the other ore zones (Hangingwall, Main and Deep Zones) have been described by Naldrett & Kullerud (1967), Cowan (1968), Abel *et al.* (1979), Coats & Snajdr (1984), and those of the Deep Copper Zone, by Li & Naldrett (1989, 1990), and are only briefly summarized here. Disseminated sulfides of the Hang-

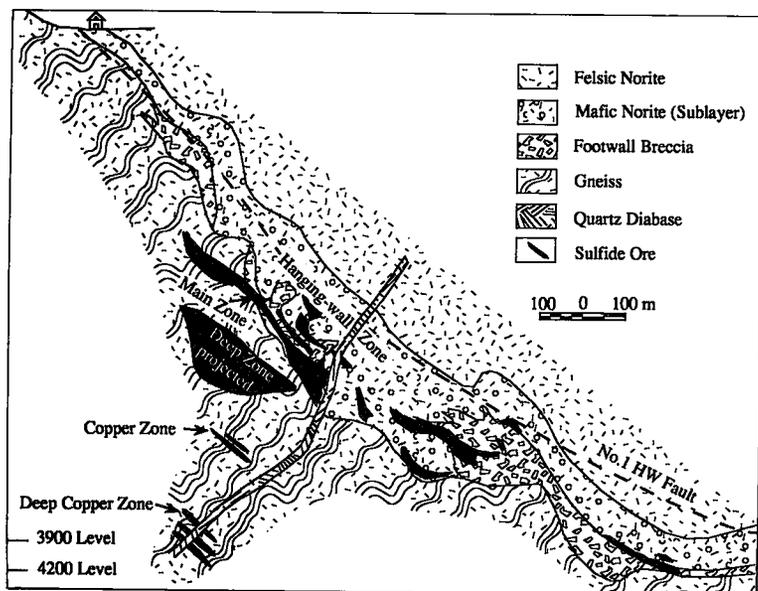


FIG. 2. Vertical cross-section through the Strathcona mine (6280E, looking east).

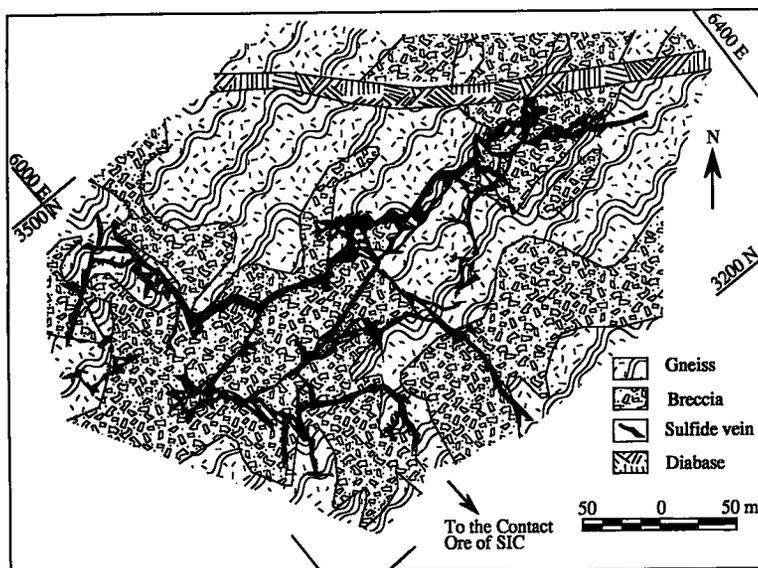


FIG. 3. Geological map of the Deep Copper Zone (3900 Level).

ingwall 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 sulfide emplaced in fractures within footwall gneiss. Very rich stringers of massive chalcopyrite and cubanite, the Copper and Deep Copper Zones, occur between 100 and 500 meters into the footwall.

The Deep Copper Zone consists of a complex system of veins (Fig. 3). The host rocks are Archean gneisses that were extensively brecciated to form the Sudbury breccia prior to the intrusion of the SIC. Quartz diabase dykes cut the Archean gneiss, Sudbury breccia and the sulfide veins. Although the contacts of the veins are sharp, chalcopyrite is dispersed a distance of several millimeters to several centimeters into the wallrocks. The dispersal was commonly accompanied by chlorite and epidote alteration, which gave rise to dark selvages along the sulfide veins. Typical hydrothermal minerals, such as quartz, calcite and epidote, occur in small branching veinlets or at the terminations of the main veins. There is no evidence of the replacement of wallrock along the veins. The vein system seems to occupy a complex series of fractures.

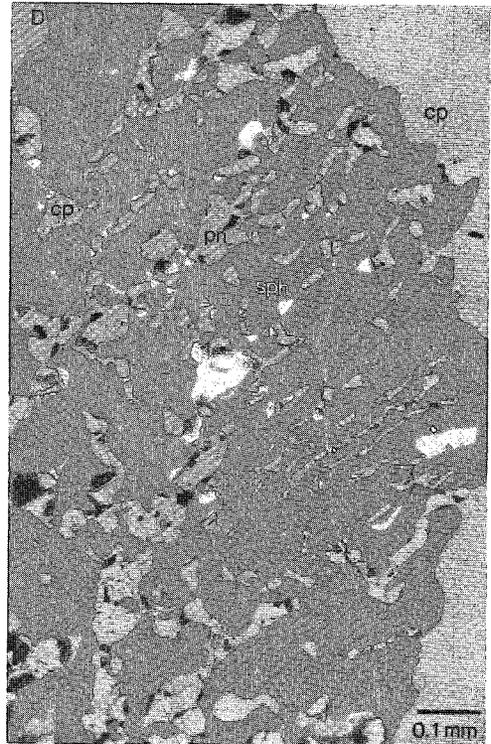
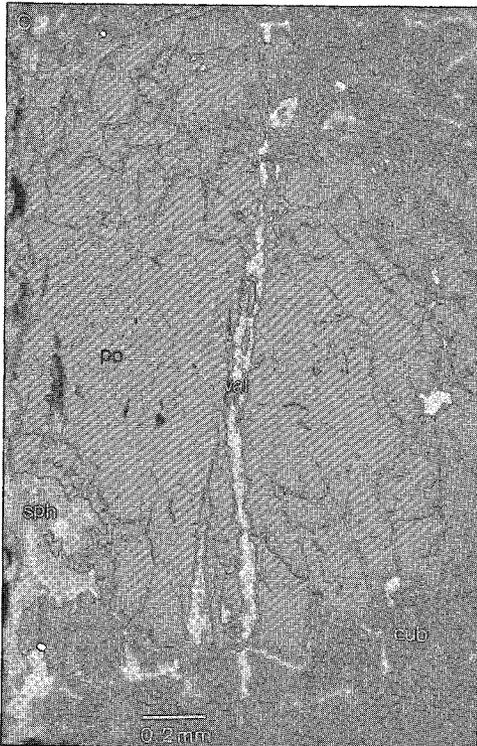
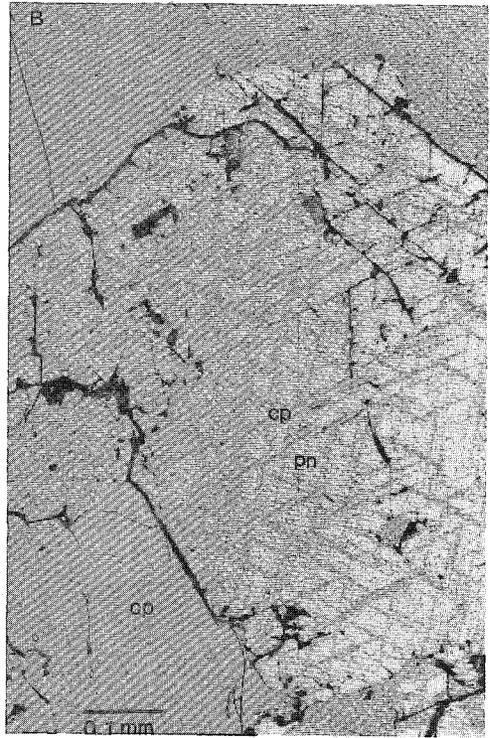
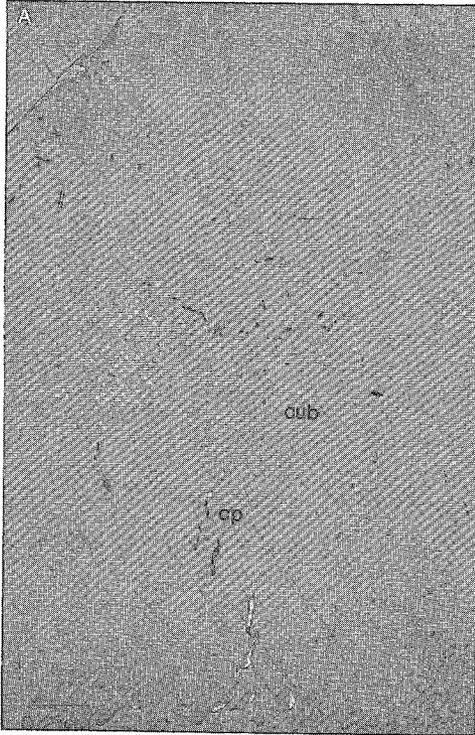
ANALYTICAL TECHNIQUES

The first stage of the investigation involved examining polished sections of 98 ore samples collected from the 3900 level of the Deep Copper Zone. The textural relationships of the major ore minerals were recorded.

The PGM, tellurides and bismuth chloride were identified by back-scattered electron imagery using a JEOL 840 scanning electron microscope (SEM) and by energy-dispersion X-ray analysis (EDA) using a PGT-4 system. The compositions of the PGM were determined using a CAMECA SX-50 electron microprobe operated at 20 or 30 kV, with a specimen current of 30 nA. The following X-ray lines and standards were used: PtM α and SnL α , PtSn; PdL α and BiM α , PdBi; TeL α , PdTe; PbM α , PbTe; AuL α , Au; AgL α , AgBiSe $_2$; AsK α , Pd $_5$ (As,Sb) $_2$; SbL α , NiSb $_2$; ClK α , tugtupite. Counting periods ranged from 20 to 50 seconds.

COMMON MINERALS

Chalcopyrite and cubanite are the predominant minerals of the veins. Chalcopyrite commonly occurs as coarse grains, and cubanite, as intergrown laminae (Fig. 4A) or irregular massive patches. Pentlandite is a minor mineral in the zone, but some portions of the veins contain spectacular blocky patches of the crystals up to 15 cm across. Large grains of pentlandite have been extensively replaced by chalcopyrite and cubanite along cleavage planes and irregular cracks (Fig. 4B). Pentlandite of exsolution origin in cubanite was reported to be present in the Deep Copper Zone by Springer (1989). Both exsolution-related and blocky types of pentlandite in the Deep Copper Zone were found to contain less nickel than pentlandite from the Main Zone ore (Springer 1989).



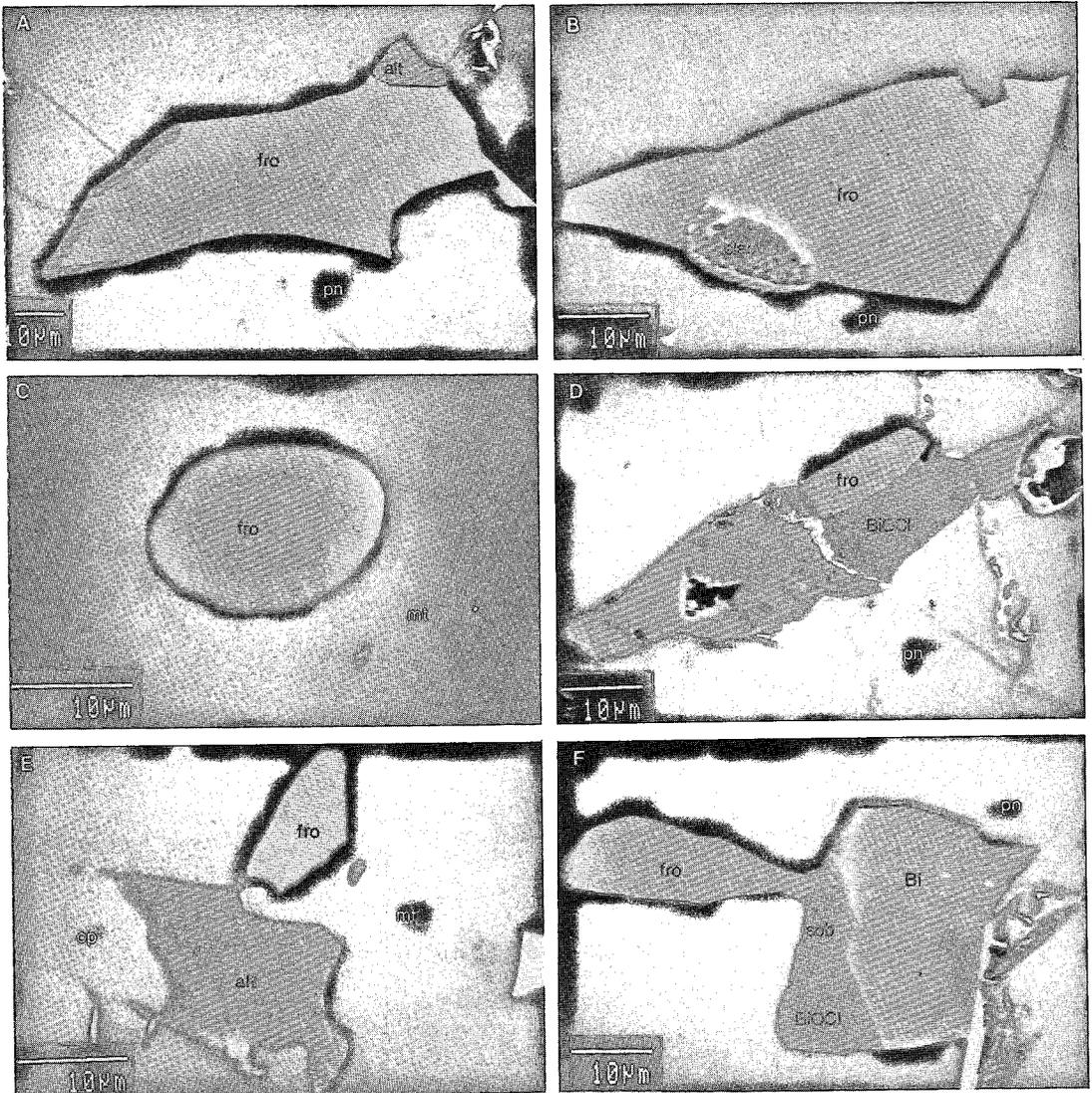


FIG. 5. Photomicrographs (secondary electron image) of froodite with its host minerals and other PGM. A. Anhedra froodite (fro) associated with altaite (alt) occurs in a microfracture in pentlandite (pn). B. Anhedra froodite, associated with electrum (elec), occurs in pentlandite. C. An oval inclusion of froodite occurs along a microfracture in pentlandite. D. Subhedra froodite, associated with bismoclite (BiOCl), occurs along a microfracture in pentlandite. E. A grain of froodite, associated with altaite, occurs between chalcopyrite and magnetite. F. An irregular grain of froodite, associated with sobolevskite (sob), bismoclite (BiOCl) and native bismuth, occurs in a microfracture in pentlandite.

FIG. 4. Textural relations of ore minerals. A. Cubanite (cub) exsolution laminae in chalcopyrite (cp). B. Pentlandite (pn) is replaced along its cleavages by chalcopyrite (cp). C. Pyrrhotite (po), extensively replaced by chalcopyrite (cp) and cubanite (cub), is cut by a vein of vallerite (val). On the bottom left are sphalerite (sph) and cubanite. D. Sphalerite (sph) includes pentlandite (pn) and chalcopyrite (cp).

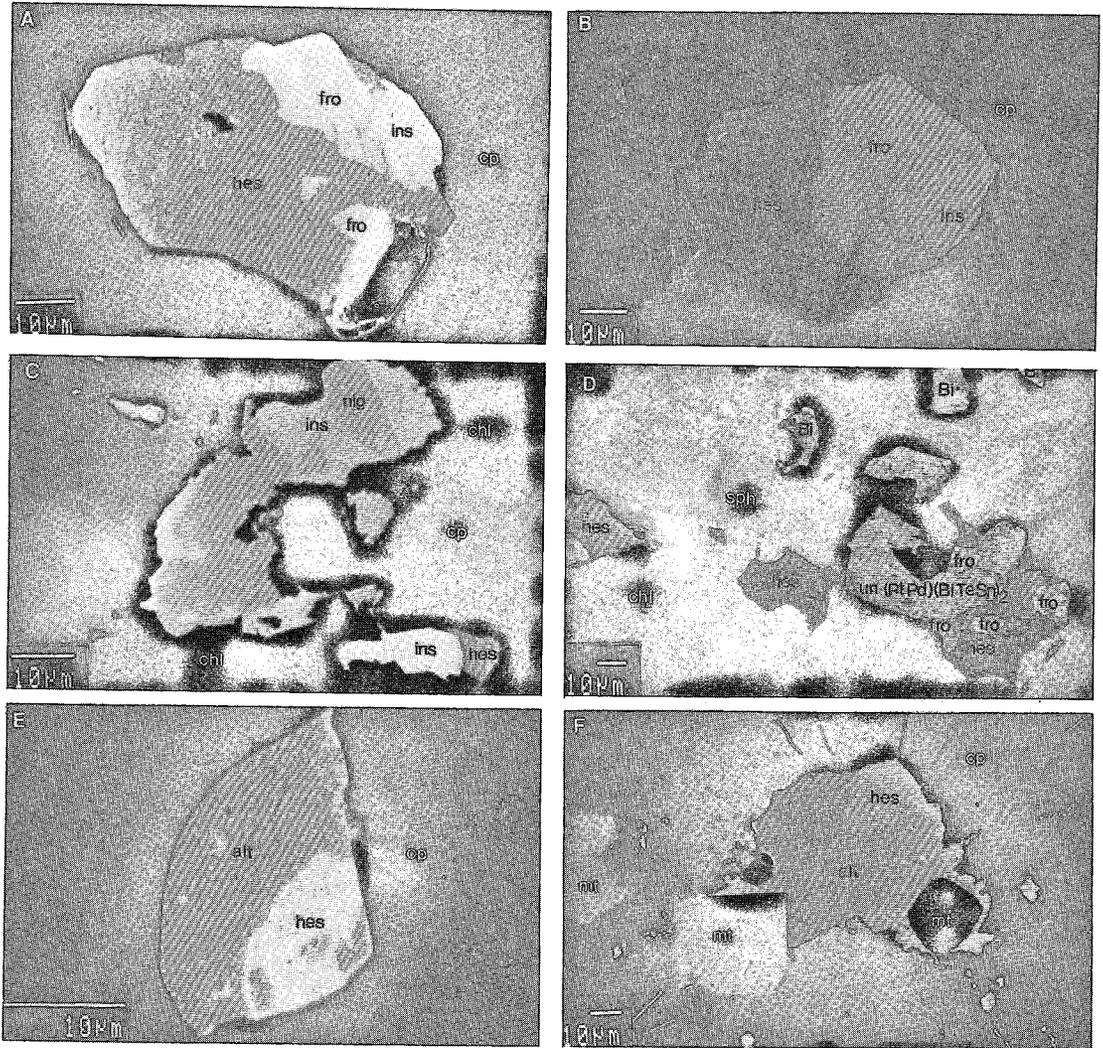


FIG. 6. Photomicrographs (secondary electron image) of insizwaite (ins), altaite (alt) and hessite (hes) with other PGM. A. Insizwaite, associated with froodite (fro) and hessite, occurs in chalcopyrite (cp). B. Insizwaite, associated with froodite and hessite, occurs in chalcopyrite. C. Insizwaite, associated with niggliite and hessite, occurs between chalcopyrite and chlorite (chl) and in a microfracture at the top left. D. Froodite, associated with a (Pt,Pd)(Bi,Te,Sn) mixture, hessite and native bismuth (Bi), occurs along the grain boundaries of sphalerite (sph), chalcopyrite and chlorite. E. Altaite and hessite occur in chalcopyrite. F. Hessite and altaite occur in radial microfractures in chalcopyrite. The dark subhedral grains are magnetite (mt).

Pyrrhotite occurs as irregular patches or narrow bands in the veins. Extensive replacement by chalcopyrite and cubanite has left most of the grains as isolated relics (Fig. 4C). Springer (1989) reported the presence of exsolution pyrrhotite in chalcopyrite from the Deep Copper Zone. His data indicate that this type of pyrrhotite has a lower Ni content than the pyrrhotite from the Main Zone ore.

Bornite occurs as patches in small veinlets of chalcopyrite that have developed chlorite and epidote alteration

at the margins. Anhedral grains of bornite (up to 1 mm in diameter) commonly enclose hematite and chalcopyrite. Some of the grains have been replaced by covellite along grain boundaries.

Magnetite is present as subhedral to euhedral grains up to several millimeters in diameter. It may be replaced by chalcopyrite and cubanite along the edges.

Although it is only a minor constituent of the ore, massive millerite occurs in patches, commonly at ex-

TABLE 1. ELECTRON-MICROPROBE DATA ON FROODITE

Sample	Elements wt %					Atomic Proportions					
	Pd	Pt	Bi	Te	Total	Pd	Pt	Σ	Bi	Te	Σ
R-9	20.94	0.31	78.77	nd	100.02	0.99	0.01	1.00	1.90	nd	1.90
R-12 a	19.88	0.09	78.90	0.16	99.02	1.00	0.00	1.00	2.02	0.01	2.03
R-12 b	21.08	nd	78.28	nd	99.36	1.00	nd	1.00	1.89	nd	1.89
898-2	20.56	0.87	80.21	nd	101.64	0.98	0.02	1.00	1.94	nd	1.94
898-5A a	21.91	nd	79.33	nd	101.24	1.00	nd	1.00	1.84	nd	1.84
898-5A b	21.87	0.03	80.25	nd	102.15	1.00	0.00	1.00	1.87	nd	1.87
898-5A c	21.58	nd	78.55	nd	100.12	1.00	0.00	1.00	1.85	nd	1.85
R-11 a	19.45	0.96	79.25	nd	99.95	0.97	nd	1.00	2.02	nd	2.02
R-11 b	19.07	0.42	80.10	nd	99.63	0.99	0.01	1.00	2.12	nd	2.12

nd: not detected.

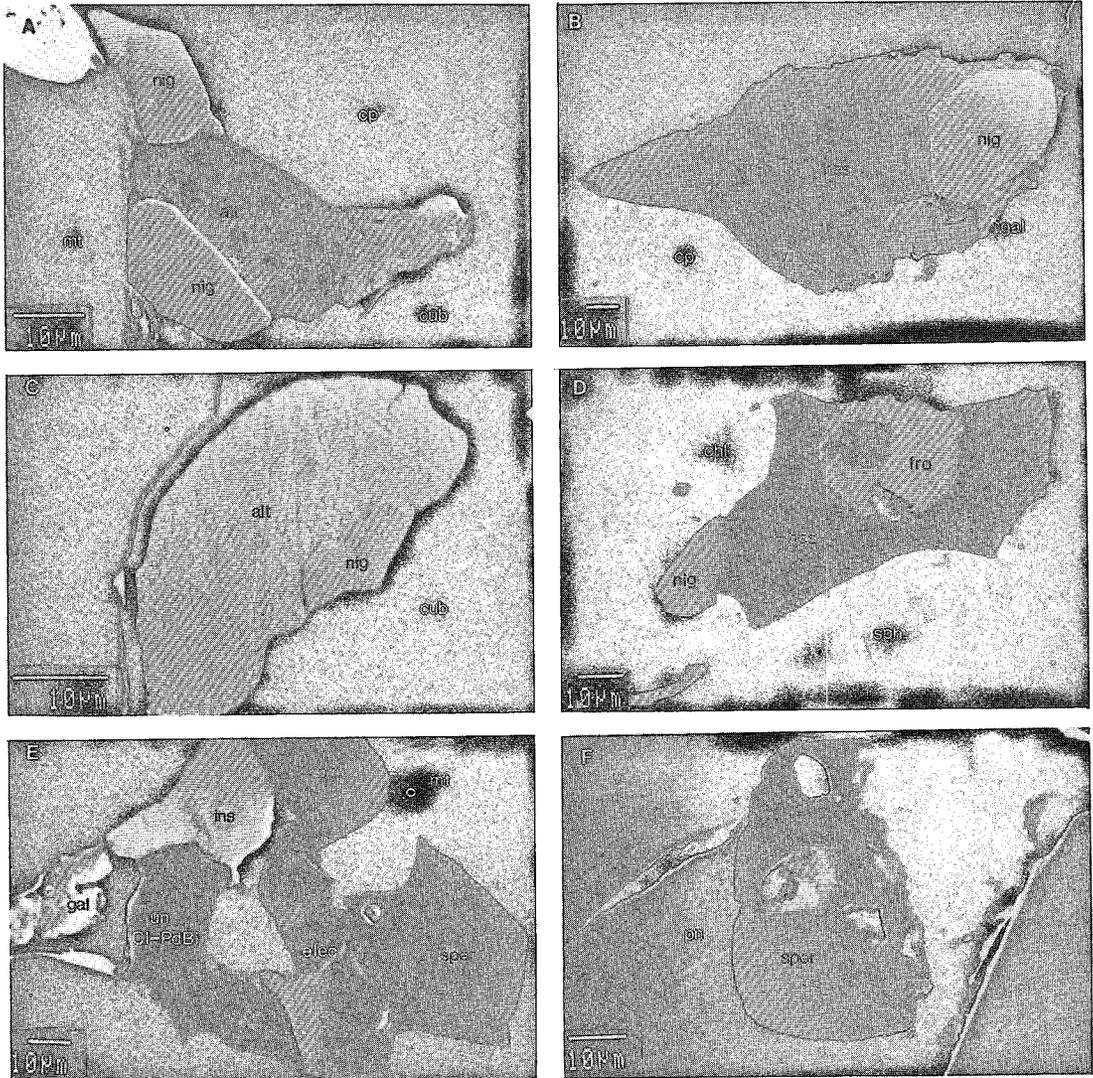


FIG. 7. Photomicrographs (secondary electron image) of niggliite (nig) associated with altaite (alt), hessite (hes) and other PGM. A. Two subhedral grains of niggliite, associated with altaite, occur in a microfracture along the grain boundaries of chalcopyrite (cp), cubanite (cub) and magnetite (mt). B. A subhedral grain of niggliite, associated with hessite and galena (gal), occurs along a microfracture in chalcopyrite. C. A anhedral grain of niggliite, associated with altaite, occurs along a microfracture in cubanite. D. Niggliite, associated with hessite and froodite, occurs between sphalerite (sph) and chlorite (chl). E. Two grains of sperrylite (sper), associated with insizwaite (ins), electrum (elec) and a Cl-bearing Pd-Bi sulfide? (un Cl-Pd-Bi), occur in a microfracture in magnetite. F. A sperrylite grain occurs in a microfracture in pentlandite (pn).

tremities, where the vein narrows and pinches out. Quartz and epidote are commonly found associated with millerite.

Minor sphalerite is evenly distributed throughout the sulfide veins. It occurs as irregular patches and usually contains numerous inclusions of pentlandite, chalcopyrite and cubanite (Fig. 4D). Additional minor and trace minerals identified with the ore microscope include mackinawite, covellite, valleriite, mawsonite, hematite and galena.

PLATINUM-GROUP MINERALS

Froodite, PdBi₂

Most of froodite grains are present in pentlandite and magnetite (Fig. 5). They vary in size from less than 5 ×

10 to 20 × 50 μm. They occur as anhedral, locally subhedral grains in the microfractures of the host minerals, but one grain is an oval inclusion in magnetite (Fig. 5C). Except for the inclusion in magnetite, all of the others are associated with rare minerals such as altaite, electrum, native bismuth, bismoclite, hessite

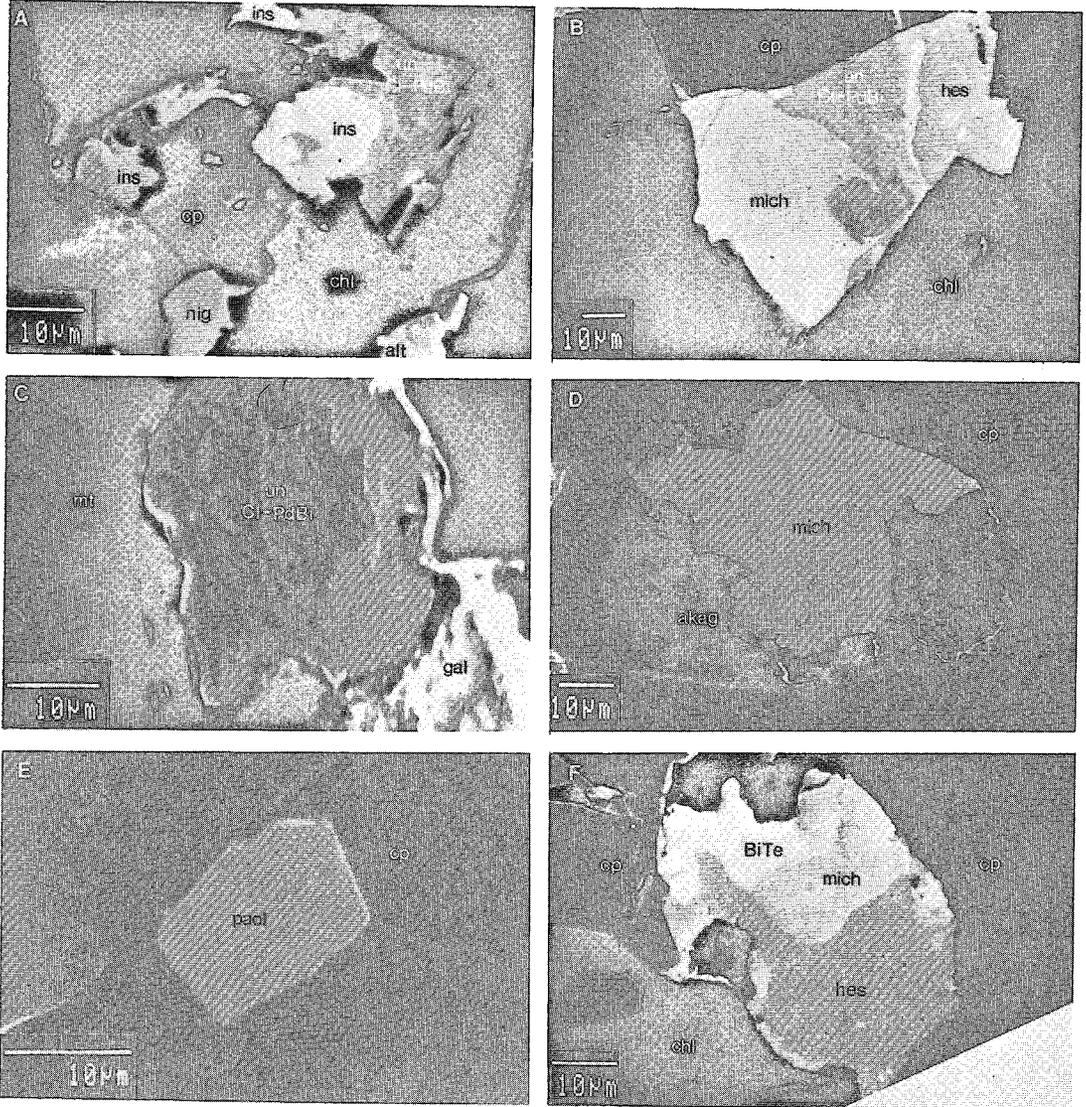


FIG. 8. Photomicrographs (secondary electron image) of michenerite and paolovite with other PGM. A. A grain of Pd-Bi chloride (un Cl-PdBi), associated with niggliite (nig), occurs between chalcopyrite (cp) and chlorite. B. Michenerite (mich), associated with Pd-Bi chloride and hessite (hes), occurs between chalcopyrite and chlorite. C. Pd-Bi chloride with ring texture occurs in a microfracture in magnetite (mt). D. Irregular michenerite occurs within a patch of acicular akaganeite (akag), cut by a microfracture filled by iron oxides, in chalcopyrite. E. Euhedral paolovite (paol) occurs along a microfracture in chalcopyrite. F. Michenerite, associated with hessite and tellurobismuthite (BiTe), occurs in the microfractures between chalcopyrite and chlorite.

TABLE 2. ELECTRON-MICROPROBE DATA ON INSIZWAITE

Sample	Elements wt. %						Atomic Proportions						
	Pt	Pd	Bi	Te	Sn	Total	Pt	Pd	Σ	Bi	Te	Sn	Σ
R-9 a	32.88	1.43	57.27	10.08	0.85	102.50	0.93	0.07	1.00	1.51	0.43	0.04	1.98
R-9 b	33.13	0.75	60.81	5.01	0.02	99.71	0.96	0.04	1.00	1.64	0.22	0.00	1.86
R-16 a	31.44	2.01	59.74	6.07	0.40	99.67	0.89	0.11	1.00	1.59	0.26	0.02	1.87
R-16 b	31.26	2.08	59.78	7.76	0.43	101.31	0.89	0.11	1.00	1.59	0.34	0.02	1.95
898-2	31.80	1.64	60.13	7.12	1.00	101.70	0.91	0.09	1.00	1.61	0.31	0.05	1.97
R-11 a	29.08	1.34	60.97	6.93	0.92	98.23	0.92	0.08	1.00	1.85	0.34	0.05	2.19
R-11 b	30.36	1.07	61.18	5.93	0.57	99.11	0.94	0.06	1.00	1.78	0.28	0.03	2.09
R-11 c	32.07	0.76	62.23	4.57	0.16	99.78	0.96	0.04	1.00	1.74	0.21	0.01	1.96
SPR-1*	28.70	3.27	54.60	12.00	-	98.50	0.83	0.17	1.00	1.47	0.53	-	2.00
-2	32.30	-	55.90	8.85	0.55	97.50	1.00	-	1.00	1.62	0.42	0.03	2.07
-3	36.70	-	31.10	16.10	11.20	95.10	1.00	-	1.00	0.79	0.67	0.50	1.96
-4	36.20	-	31.90	20.30	8.40	96.80	1.00	-	1.00	0.38	0.82	0.86	2.06

*SPR-1, 2, 3 & 4 (Springer 1989). SPR-1 & 2 were reported by the author as moncheite, and SPR-3 & 4 as niggliite. SPR-1, 2 & 3 actually calculate out to insizwaite, and SPR-4 to moncheite (see text for discussions).

(Figs. 6A, B, D), and PGM such as sobolevskite (Fig. 5F) and insizwaite (Figs. 6A, B).

Results of nine analyses performed on froodite (Table 1) show that the mineral ranges in composition from pure PdBi₂ to (Pd,Pt)(Bi,Te)₂, but that extent of substitution of Pt for Pd and of Te for Bi is not significant. All of the data are in good agreement with those for froodite from other deposits at Sudbury, reported by Cabri & Laflamme (1976).

Insizwaite, Pt(Bi,Sb)₂

Six grains of insizwaite are present in our samples from the Deep Copper Zone. Cabri & Laflamme (1976) reported the occurrence of this mineral in the neighboring Coleman deposit. They also investigated several other deposits at Sudbury, including Levack West, Creighton, Crean Hill, Victoria, Copper Cliff, Frood and Falconbridge deposits, but no insizwaite was found.

The insizwaite in the Deep Copper Zone is invariably associated with other PGM (froodite, niggliite, sperrylite and Pd-Bi chloride), electrum and hessite (Figs. 6A, B, C, 7E, 8A). The insizwaite grains vary in size from 3 × 5 to 20 × 30 μm. They are anhedral; several are irregular. Although this fact is not well shown in the SEM

photomicrographs, all the grains of insizwaite have been found to be microfracture-related.

Results of eight analyses of insizwaite (Table 2) indicate that the mineral has the general formula (Pt,Pd)(Bi,Te,Sn)₂, with Pt >> Pd and Bi >> Te > Sn. Concentrations of the elements are similar to those in insizwaite from the Coleman deposit, reported by Cabri & Laflamme (1976). Three compositions (SPR-1, 2, 3), which were originally reported as "moncheite" (SPR-1, 2) and as "niggliite" (SPR-3) by Springer (1989), are listed in the table for comparison. They actually correspond to insizwaite. Another composition of Springer's "niggliite" (SPR-4) also is listed in Table 2. This one actually corresponds to bismuthian stannian moncheite. The author described his "moncheite" and "niggliite" as creamy white and anisotropic. There are some contradictions between the optical descriptions and the analytical data. First of all, if the "moncheite" is indeed a variety of insizwaite, it cannot be anisotropic. Our insizwaite is clearly isotropic, similar to that reported by Cabri & Laflamme (1976). Another problem is that niggliite in our samples has a distinctive pleochroism, from pinkish white to pale blue, and strong birefractance. The creamy white color of Springer's description does not fit niggliite.

TABLE 3. ELECTRON-MICROPROBE DATA ON NIGGLIITE

Sample	Elements wt. %						Atomic Proportions						
	Pt	Pd	Sn	Sb	Bi	Total	Pt	Pd	Σ	Sn	Sb	Bi	Σ
Ap-4A a	60.74	0.92	37.58	0.24	0.40	99.88	0.97	0.03	1.00	0.99	0.006	0.006	1.002
Ap-4A b	59.90	1.07	37.34	0.10	0.64	99.05	0.97	0.03	1.00	0.99	0.002	0.010	1.002
Ap-4A c	60.61	0.93	37.57	0.15	0.10	99.36	0.97	0.03	1.00	0.99	0.004	0.002	0.996
Ap-4B	59.25	1.28	33.69	2.83	2.57	99.62	0.96	0.04	1.00	0.90	0.070	0.040	1.010
R-16	60.42	0.62	37.31	0.78	0.18	99.31	0.98	0.02	1.00	1.00	0.020	0.003	1.023

Niggliite, PtSn

Eight grains of niggliite are present in our samples. All are subhedral (Figs. 7A, B, C, D, 8A), with sizes ranging from 5×10 to $30 \times 50 \mu\text{m}$. They are associated with altaite and hessite, situated along the boundaries between sulfides and chlorite (Figs. 7D, 8A) and in microfractures in chalcopyrite, cubanite and magnetite (Figs. 7A, B, C). Results of electron-microprobe analyses are listed in Table 3. There are minor amounts of Pd replacing Pt, and Bi and Sb replacing Sn.

Like insizwaite, niggliite has been found only from the Deep Copper Zone in this study and from the Coleman deposit at Sudbury (Cabri & Laflamme 1976).

Michenerite, (Pd,Pt)BiTe

Michenerite occurs as anhedral grains ranging from less than $10 \mu\text{m}$ to more than $30 \mu\text{m}$ in diameter (Figs. 8B, D, F). It is present in association with hessite, tellurobismuthite and a Pd-Bi chloride (Figs. 8B, F), situated along grain boundaries between chalcopyrite and chlorite. One grain occurs within a patch of acicular iron hydroxides cut by a microfracture (Fig. 8D). The michenerite has an irregular shape and seems to have been deformed.

The compositions obtained for michenerite are listed in Table 4. The stoichiometric values are not as good as for the other minerals. We checked for the presence of Ni, but did not detect it. The contents of Pt in michenerite from the Deep Copper Zone range from 0.15 to 8.67 wt.% (Table 4), which are similar to those from the Levack West and Coleman deposits (Cabri & Laflamme 1976). Cabri & Laflamme (1976) reported differences between michenerite from the North and South Range deposits at Sudbury. Their data indicate that michenerite from the North Range is Pt-bearing, and that from the South Range is not.

Sperrylite, PtAs₂

Three grains of sperrylite were observed in our

TABLE 4. ELECTRON-MICROPROBE DATA ON MICHENERITE

Sample	Elements wt.%					Atomic Proportions					
	Pd	Pt	Bi	Te	Total	Pd	Pt	Σ	Bi	Te	Σ
R-16	17.40	8.67	45.39	28.17	99.63	0.79	0.21	1.00	1.04	1.06	2.10
L-25 a	21.86	0.85	47.74	29.20	99.70	0.98	0.02	1.00	1.09	1.09	2.18
L-25 b	21.59	0.65	46.92	28.98	99.14	0.98	0.02	1.00	1.08	1.09	2.19

samples. Two grains are associated with insizwaite, a Pd-Bi chloride, electrum and galena in a microfracture in magnetite (Fig. 7E). The other grain occurs in a cavity in pentlandite (Fig. 7F). They are all anhedral and about $25 \times 50 \mu\text{m}$ in size.

One analysis shows that sperrylite from the Deep Copper Zone is close to ideal PtAs_2 , with minor Sb (Table 5). Cabri & Laflamme (1976) reported that this mineral is a principal Pt mineral in the South Range, but is sparse in deposits of the North Range.

Sobolevskite, PdBi

Only one very small grain ($5 \times 10 \mu\text{m}$) of sobolevskite is present in our samples. This is the first report of sobolevskite at Sudbury. It is intergrown with froodite, native bismuth and bismoclitite (BiOCl), in a crack in pentlandite (Fig. 5F). Its composition is listed in Table 5.

Paolovite, Pd₂Sn

One single euhedral grain of paolovite ($10 \times 15 \mu\text{m}$) occurs along a microfracture in chalcopyrite (Fig. 8E). This is its first reported occurrence from Sudbury. Its composition is listed in Table 5.

(Pt,Pd)(Bi,Te,Sn) mixture?

One irregular grain of this compound ($10 \times 30 \mu\text{m}$) is present in association with froodite, hessite and native bismuth (Fig. 6D). It occurs along the contact between sphalerite and chlorite. It has a poor polished surface, a

TABLE 5. ELECTRON-MICROPROBE DATA ON PAOLOVITE, SPERRYLITE AND SOBOLEVSKITE

Sample	Elements wt.%							Atomic Proportions						
	Pd	Pt	Sn	As	Sb	Bi	Total	Pd	Pt	Sn	As	Sb	Bi	
L-5:														
Paolovite	63.94	nd	35.09	-	-	nd	99.03	2.00	nd	0.98	-	-	nd	
898-5:														
Sperrylite	nd	57.11	nd	42.29	0.57	nd	99.97	nd	1.00	nd	1.91	0.02	nd	
898-5A:														
Sobolevskite	34.7	nd	nd	-	-	63.9	98.53	1.07	nd	nd	-	-	1.00	

nd: not detected; -: not determined.

TABLE 6. ELECTRON-MICROPROBE DATA ON ONE GRAIN OF (Pt,Pd)(Bi,Te,Sn)

Elements wt. %							Atomic Proportions					
Pt	Pd	Bi	Te	Sn	Total	Pt	Pd	Σ	Bi	Te	Sn	Σ
35.02	3.39	23.01	21.38	17.23	100.04	0.85	0.15	1.00	0.52	0.79	0.69	2.00
33.52	4.05	25.98	20.71	16.36	100.61	0.82	0.18	1.00	0.59	0.77	0.66	2.02
12.65	13.53	57.74	9.17	6.86	99.99	0.34	0.66	1.00	1.44	0.37	0.30	2.11
25.19	8.10	40.77	15.56	12.06	101.68	0.63	0.37	1.00	0.95	0.59	0.50	2.04
39.46	1.40	15.01	24.20	19.26	99.30	0.94	0.06	1.00	0.33	0.88	0.75	1.96
38.15	2.01	18.40	23.35	18.52	100.42	0.91	0.09	1.00	0.41	0.85	0.73	1.99

from sample R-12.

greyish white color, and is weakly anisotropic in reflected light. It appears slightly inhomogeneous with back-scattered electron imagery. The composition of this compound varies from location to location (Table 6). The Pt content increases with Bi, and that of Te and Sn increases with Pt. Four of the analyses show Te > Sn > Bi. The other two analyses show Bi > Te > Sn. We suspect that the variation may be due to intergrowth of different species. One of the minerals could be froodite because the ratio Pd/Bi of the unknown compound is close to that of froodite. Another phase could be niggliite, because niggliite has similar Pt/Sn ratio to the unknown compound and is also the only Pt- and Sn-bearing phase found in the ores. However, this explanation would require a third constituent, an almost pure Te phase, which has not been found in the ore. An alternative is that the unknown compound is a mixture of froodite with another new phase, Pt(Te,Sn)₂. The third possibility is that the unknown compound may be a new mineral with the formula (Pt,Pd)(Bi,Te,Sn)₂, with Pd replacing Pt and Te, and Sn replacing Bi inhomogeneously.

Unnamed Pd-Bi chloride

Three irregular grains of this unnamed compound are present in our samples. One grain overgrows insizwaite at the contact between chalcopyrite and chlorite (Fig. 8A). The second grain is intergrown with michenerite and hessite (Fig. 8B). The third grain occurs alone in a fracture in magnetite (Fig. 8C). In reflected light, this compound is pleochroic from pinkish brown to pale brown. It contains 3.66 to 5.96% Cl and about 10% (by difference) O or OH (Table 7). A wavelength-dispersion spectrum of this phase was examined for the presence of additional elements. No elements were observed other than those listed in Table 7, plus oxygen. Although some of the grains do not look homogeneous, the compositions of different spots do not vary greatly (Bi and Pt, <10%). Data on a Pd-Bi chloride (Pd₄Bi₅Cl₃) from the (former) Soviet Union (Karpenkov *et al.* 1981) also are listed in the table for comparison. The Pd-Bi chloride

from the Deep Copper Zone seems to have higher Pd and lower Bi.

Although the findings differ in detail, the experimental data (Orlova *et al.* 1987, Hsu *et al.* 1991) and theoretical calculations (Mountain & Wood 1988, Wood *et al.* 1989, Sassani & Shock 1990) suggest that Pd can be transported as a chloride complex. The discovery of the Cl-bearing Pd compound in association with other PGM from the Deep Copper Zone is of significance because it has a bearing on the possible importance of Cl as a complexing agent.

Unnamed Cl-bearing Pd-Bi sulfide?

Three grains of this mineral (up to 15 × 50 μm) occur in association with bismoclite (BiOCl) in fractures in magnetite. One grain is associated with insizwaite, sperrylite and electrum in the fractures in magnetite (Fig.

TABLE 7. ELECTRON-MICROPROBE DATA ON Pd-BI CHLORIDE AND BISMOCLITE

Sample	Pd	Pt	Bi	Te	Pb	Cl	Total (%)
<i>Pd, Bi, O, OH, Cl compound? (3 grains, 3 analyses each grain)</i>							
R-16	33.56	1.21	51.62	0.53	0.47	3.66	91.05
	27.59	0.92	58.02	0.04	0.61	3.76	90.95
	30.44	0.92	54.17	0.50	0.57	4.58	91.16
	34.31	1.32	44.21	0.06	1.14	5.01	86.03
	32.90	0.84	49.39	0.04	1.29	5.63	90.08
	32.88	0.95	48.03	0.03	1.47	5.59	88.96
	32.17	0.95	53.10	nd	1.14	5.96	92.32
	29.50	1.97	54.32	0.20	1.07	5.59	92.64
	35.05	1.15	46.13	0.06	1.09	4.98	88.46
	<i>Pd₄Bi₅Cl₃*</i>						
	24.50	2.07	64.10			6.43	97.10
<i>Bismoclite, BiOCl (2 grains)</i>							
898-5A			78.43	0.33		11.88	90.65
			79.66	0.42		11.46	91.62
<i>Ideal bismoclite (BiOCl)</i>							
			80.25			13.61	93.86

* It also contains 0.78 % of Fe and 0.27 % of Ni (Karpenkov *et al.* 1981). nd: not detected.

TABLE 8. ELECTRON-MICROPROBE DATA ON Pd-Bi SULFIDE⁷

Pd	Pt	Bi	Pb	Fe	Ni	Zn	S	Cl	Total (%)
50.64	0.40	21.42	0.72	1.28	0.51	0.52	11.74	1.19	88.42
45.65	0.34	27.24	0.87	2.03	1.38	1.79	9.35	1.36	90.00
53.88	0.39	23.88	0.53	1.16	0.34	0.07	8.05	1.55	89.86

Note: Three grains one analysis each grain, all grains from sample R-9

7E). In reflected light, this compound is grey and isotropic. Compositions are listed in Table 8. The concentration of sulfur ranges from 11.74 to 8.05 wt.%, and that of chlorine, from 1.19 to 1.55 wt.%. A wavelength-dispersion spectrum of this phase was carefully examined; no other elements were observed except for those listed in Table 8 plus oxygen.

OTHER RARE PHASES

Bismoclite, BiOCl

Two grains of this mineral are present in our samples, one associated with froodite (Fig. 5D), and the other with froodite, native bismuth and sobolevskite (Fig. 5F). The former is deformed, cut by microfractures in pentlandite. Their compositions are listed along with that of ideal bismoclite in Table 7. Bismoclite is not a common mineral. It usually occurs as a secondary phase by replacing bismutite $[\text{Bi}_2(\text{CO}_3)_2\text{O}_2]$ or native bismuth (Palache *et al.* 1951). The textural relationships of this mineral to other PGM and native bismuth show no evidence of a secondary origin.

Altaite and hessite

Besides the occurrence in association with the PGM, altaite and hessite also occur alone in the ores (Figs. 6E, F), intergrown together within fractures in sulfides. The compositions of hessite are given in Table 9.

DISCUSSION

Mineralogical balances

To calculate a mineralogical balance of the PGE, one needs to know the bulk concentrations of the PGE, the

TABLE 9. ELECTRON-MICROPROBE DATA ON HESSITE

Sample	Te	Ag	Total (%)
R-12	37.42	61.26	98.08
R-16	37.71	61.49	99.20
898-2	37.76	61.66	99.42

modal proportion of the PGM, the compositions of the PGM, and the modal proportions of the other PGE-bearing minerals, as well as the concentrations of PGE within them. The bulk PGE content of the Deep Copper Zone, estimated from 32 analyses of massive sulfide ore, are 4419 ppb Pt and 5213 ppb Pd (Li & Naldrett 1990). The main minerals of the ore consist of chalcopyrite, cubanite, magnetite, pentlandite, pyrrhotite, millerite and bornite, in the order of their relative abundance. Because of their inhomogeneous distribution, it is difficult to obtain the modal proportions of the minerals by point counting or image analysis. An alternative is to use a normative calculation. The composition of the Deep Copper Zone, calculated from 1577 samples of massive ore analyzed by Falconbridge Limited, is 26.21% Cu, 2.17% Ni, and 32.35% S. If all of the Ni occurs as pentlandite, this amounts to 5.71 wt.% pentlandite. This is a maximum value because the ore also contains minor amounts of another Ni-bearing mineral, millerite. Copper occurs as either chalcopyrite, cubanite or bornite. Examinations of polished sections indicate that bornite is present in trace amounts only, and that chalcopyrite and cubanite are generally associated with each other in a ratio of 3:1. If 3/4 and 1/4 of the Cu are assigned to form chalcopyrite and cubanite, respectively, we have 61.7 wt.% chalcopyrite and 20.6 wt.% cubanite in the ore. Assignment of the rest of the S to form pyrrhotite gives 4.5% pyrrhotite. The calculated modal proportions of chalcopyrite, cubanite, pentlandite and pyrrhotite together total 92.5 wt.%. The addition of another 6 wt.% of magnetite, based on estimates from microscopic observations, brings the total up to 98.5 wt.%, which comes close to accounting for all of the ore.

The concentrations of Pt and Pd in the sulfides and magnetite, determined by accelerator mass spectrometry (AMS), are: 1047 ppb Pd in pentlandite, less than 25 ppb Pd in chalcopyrite, cubanite, millerite and magnetite, and less than 4 ppb Pt in all of the minerals. If the modal wt.% values of the minerals calculated above are used, less than 1.2% of the Pd can be accounted for in pentlandite, and less than 0.4% of the Pd can be accounted for in chalcopyrite, cubanite, millerite and magnetite. The sulfides, together with magnetite, can therefore account for less than 0.1% of the Pt of the ore. The calculations indicate that more than 98.4% of the Pd and more than 99.9% of the Pt in the ore must occur in other phases.

The relative abundance of Pt and Pd in the PGM can be calculated if the relative abundance of the PGM and their composition are known. The least that could be done would be to determine their relative cumulative area. Using the average composition of PGM from the Deep Copper Zone, the relative abundance of the Pt and Pd are calculated and listed in Table 10. Among PGM that have been found from the Deep Copper Zone, the most important Pd minerals are froodite (42.5% of the Pd) and michenerite (21.4% of the Pd), and the most important Pt minerals are sperrylite (42.9% of the Pt)

TABLE 10. DISTRIBUTIONS OF Pt and Pd IN PGM

Minerals	Grain grains	Grain size (μm^2)		Cumulative area (μm^2)	PGM dist.	Pt dist.	Pd dist.	
		Ave.	Range					
froodite	14	34.15	386	25-1400	5401	27.08	0.36	45.25
niggliite	8	19.51	344	50-1350	2750	13.54	36.68	0.80
insizwaite	6	14.63	242	25-600	1450	7.27	10.16	0.61
sperrylite	3	7.32	1133	700-1500	3400	17.04	42.91	-
michenerite	3	7.32	1167	200-2100	3500	17.55	2.62	21.42
Pd-Bi chloride (Pt,Pd)(Bi,Te,Sn) mixture	2	4.88	690	300-1080	1380	6.92	-	13.33
Pd-Bi sulfide?	1	2.44	825	-	825	4.14	-	12.37
psalovite	1	2.44	192	-	192	0.96	-	3.86
sobolevskite	1	2.44	50	-	50	0.25	-	0.63
	41	100			19998	100	100	100

Note: Ave. = average, dist. = distribution.

and niggliite (36.7% of the Pt). Sperrylite has been reported also to be the principal Pt mineral in the mill product from Sudbury (Cabri & Laflamme 1984). Michenerite, which is the second most important Pd mineral in the Deep Copper Zone, is the most important one in the mill product from Sudbury (Cabri & Laflamme 1984).

Implications as to paragenesis

Pyrrhotite, pentlandite and magnetite are the principal ore minerals of the Hangingwall and Main Zones (Cowan 1968). They have been interpreted as the typical phases of a primary magmatic sulfide liquid (Naldrett & Kullerud 1967, Naldrett *et al.* 1967). The minor amounts of these minerals that are present in the Deep Copper Zone are possibly the relics of the early sulfide liquid. The exsolution texture of chalcopyrite and cubanite suggests that they originally crystallized as an intermediate solid-solution (*Iss*) from a Cu-rich sulfide liquid. They subsequently exsolved from each other during cooling, as inferred from the phase diagrams for the system Fe-Cu-S (Cabri 1973, Craig & Scott 1974).

All grains of PGM, except for one inclusion of froodite in magnetite, occur at the margins of sulfides, in the microfractures of sulfides and magnetite, and between the contacts of sulfides with chlorite, suggesting that the PGM crystallized after the sulfide minerals.

The presence of Cl-bearing hydrous minerals adjacent to the sulfide veins and of high-salinity fluid inclusions in quartz associated with chalcopyrite and millerite in branching veinlets indicates that a Cl-bearing fluid was involved in the development of the vein system. The Cl-bearing minerals in the contact alteration of the veins include ferropyrrosalite (Mn^{2+} , Fe^{2+})₈ $\text{Si}_6\text{O}_{15}(\text{OH},\text{Cl})_{10}$, annite and ferro-tschemakitic hornblende. Ferropyrrosalite contains 5.66–6.54% Cl. Annite and ferro-tschemakitic hornblende contain 1.31–2.13% and 0.86–2.99% Cl, respectively.

Primary fluid inclusions in the quartz-chalcopyrite and quartz-millerite veinlets are multiphase ($\text{LVX}_1\text{X}_2\text{X}_3$), with a mean temperature of homogenization of $342 \pm 61^\circ\text{C}$. The daughter minerals identified by

SEM are Na chloride, Ca chloride, Pb-K chloride and Fe-Mn chloride. The salinity, estimated from the system of $\text{NaCl-CaCl}_2\text{-H}_2\text{O}$ (Vanko *et al.* 1988), is about 25 wt.% eq. of NaCl and 35 wt.% eq. of CaCl_2 .

The occurrence of a Pd-Bi chloride and Bi chloride (BiOCl) associated with other PGM suggests that Cl was an important component during the precipitation of the PGM. Other important components in this process include Bi, Te, As and Sn, as indicated by the compositions of the PGM.

The textural relationships of the PGM with the major ore minerals suggest that the PGE along with Te, Bi, Sn and As, may have been partitioned into a coexisting, Cl-rich fluid during the crystallization of *Iss* from a Cu-rich sulfide liquid. The PGM formed subsequently on further cooling of the fluid. An alternative interpretation is that the PGE were removed and deposited by the fluid during a later event. The patterns of distribution of the PGE in the zone indicate that they were not dispersed beyond the sulfide vein, and not enriched in the alteration zones and quartz-bearing veinlets (Li *et al.* 1992). The close relationships between the PGM and minerals filling the veins suggest that they both formed as a result of a continuous sequence of events. The progressive transition from the massive sulfide veins into the quartz-chalcopyrite veinlets in the Deep Copper Zone suggests that sulfide mineralization and hydrothermal development are not independent events. Thus it is likely that the hydrothermal phase separated as a result of the evolution (crystallization) of the liquid.

CONCLUSIONS

1. The Pt and most of the Pd in the Deep Copper Zone have been found in discrete minerals.
2. The Deep Copper Zone contains at least eight PGM species. Froodite and michenerite are the most important Pd-bearing minerals; niggliite, sperrylite and insizwaite are the most important Pt-bearing minerals.
3. The textural relationships of the PGM and their host minerals suggest that the deposition of PGM occurred during the final stage of the evolution of the sulfide liquid, which probably involved the separation of a hydrothermal fluid.
4. The compositions of the PGM indicate that their precipitation was controlled by the contents of Bi, Te, Sn As and Cl in the residual fluid.

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