

PARTITIONING OF THE PLATINUM-GROUP AND OTHER TRACE ELEMENTS IN SULFIDES FROM THE BUSHVELD COMPLEX AND CANADIAN OCCURRENCES OF NICKEL-COPPER SULFIDES¹

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ABSTRACT

Concentrations of platinum-group elements (*PGE*), Se, Te, Ag, Cd, Zn, Ga, and Ge in approximately 180 grains of pentlandite, chalcopyrite and pyrrhotite from the Bushveld Complex, Muskox intrusion (Northwest Territories), Rottenstone (Saskatchewan), Namew Lake and Cuthbert Lake (Manitoba), Wellgreen (Yukon), and St. Stephen, Mechanic and Goodwin Lake (New Brunswick) have been determined by proton microprobe. Among the coexisting pentlandite, chalcopyrite and pyrrhotite, pentlandite is the only phase that accommodates detectable levels of Pd, Rh and Ru. Concentrations attain 566 ppm Pd, 41 ppm Rh, and 61 ppm Ru. Pentlandite with high concentrations of the *PGE* appears to be restricted to *PGE*-Ni-Cu deposits and occurrences in which sulfides are disseminated in character and where the *PGE* tellurides and bismuthotellurides are not abundant platinum-group mineral species. The availability of Bi and Te appears to control the extent of *PGE* exsolution in sulfides. In pentlandite, there is a negative correlation between Se and Co, and a crude positive correlation between Se and *PGE* contents. Bi, Se and Te are equally abundant in all three phases. In general, sulfides from *PGE*-rich occurrences have Se/S ratios greater than or within the mantle range. Sulfides from *PGE*-poor Ni-Cu occurrences, such as the St. Stephen and Goodwin Lake intrusions, in which the sulfur is mainly of crustal origin, display lower Se/S ratios. Almost all analyzed grains of chalcopyrite and most of pentlandite contain detectable levels of Ag; concentrations attain 279 ppm in pentlandite and 111 ppm in chalcopyrite. Zinc seems to partition exclusively into chalcopyrite. Ga seems to prefer pentlandite, whereas chalcopyrite accommodates all available Ge.

Keywords: platinum-group elements, trace elements, element partitioning, proton microprobe, Se/S ratio, Bushveld, Ni-Cu sulfide deposits, ore genesis.

SOMMAIRE

Nous avons déterminé la concentration des éléments du groupe du platine (*EGP*) et de Se, Te, Ag, Cd, Zn, Ga et Ge dans environ 180 grains de pentlandite, chalcopyrite et pyrrhotite provenant du complexe du Bushveld, de l'intrusion du Muskox (Territoires du Nord-Ouest), et des minerais des gisements de Rottenstone (Saskatchewan), Namew

Lake et Cuthbert Lake (Manitoba), Wellgreen (Yukon), et St. Stephen, Mechanic et Goodwin Lake (Nouveau Brunswick). Là où pentlandite, chalcopyrite et pyrrhotite coexistent, seule la pentlandite semble accommoder Pd, Rh et Ru à des concentrations supérieures aux seuils de détection. Les concentrations atteignent 566 ppm de Pd, 41 ppm de Rh, et 61 ppm de Ru. La pentlandite à teneurs élevées en *EGP* semble limitée aux gisements et indices dans lesquels 1) les sulfures sont disséminés, et 2) les tellurures et bismuthotellurures des *EGP* ne sont pas répandus. La disponibilité du Bi et du Te exercerait un contrôle important sur l'exsolution des *EGP* dans ces sulfures. Dans la pentlandite, nous trouvons une corrélation négative entre Se et Co, et une faible corrélation positive entre Se et les *EGP*. Les trois phases ont sensiblement les mêmes teneurs en Bi, Se et Te. En général, les sulfures des massifs enrichis en *EGP* possèdent un rapport Se/S supérieur ou semblable à la valeur attribuée au manteau. Les sulfures des gisements de Ni-Cu à faible teneur en *EGP*, comme ceux de St. Stephen et Goodwin Lake par exemple, dans lesquels le soufre possède une origine crustale surtout, font preuve d'un rapport Se/S plus faible. Presque tous les grains de chalcopyrite que nous avons analysés, et la plupart des grains de pentlandite, possèdent des quantités mesurables d'argent; les concentrations atteignent 279 ppm dans la pentlandite et 111 ppm dans la chalcopyrite. Le zinc semble entièrement réparti dans la chalcopyrite. Le Ga semble préférer la pentlandite, tandis que la chalcopyrite accommode la totalité du Ge.

(Traduit par la Rédaction)

Mots-clés: éléments du groupe du platine, éléments traces, répartition des éléments, microsonde protonique, rapport Se/S, Bushveld, gisements de sulfures de Ni-Cu, mode de formation du minéral.

INTRODUCTION

A knowledge of the concentrations of platinum-group elements (*PGE*) in solid solution in base-metal sulfide minerals is extremely important, not only for mineral processing, but also to understand the partition of the *PGE* between solids and sulfide melts, and their distribution among base-metal sulfide minerals during subsolidus events. The proton microprobe makes *in situ* trace-element analysis of minerals possible through proton-induced X-ray emission (*PIXE*) because of its lower flux of background radiation. This technique has recently

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emerged as a complementary tool to the electron microprobe in mineralogical research (Cabri *et al.* 1984, 1985, Harris *et al.* 1984, Cousens *et al.* 1987, Remond *et al.* 1987). As a follow-up to these initial micro-PIXE studies, base-metal sulfide minerals

from selected Ni-Cu, Ni-Cu-PGE, and PGE deposits or occurrences in Canada and the Bushveld Complex of South Africa were analyzed. In addition to the new data on the distribution of PGE and other trace elements, we hope that the trace-element

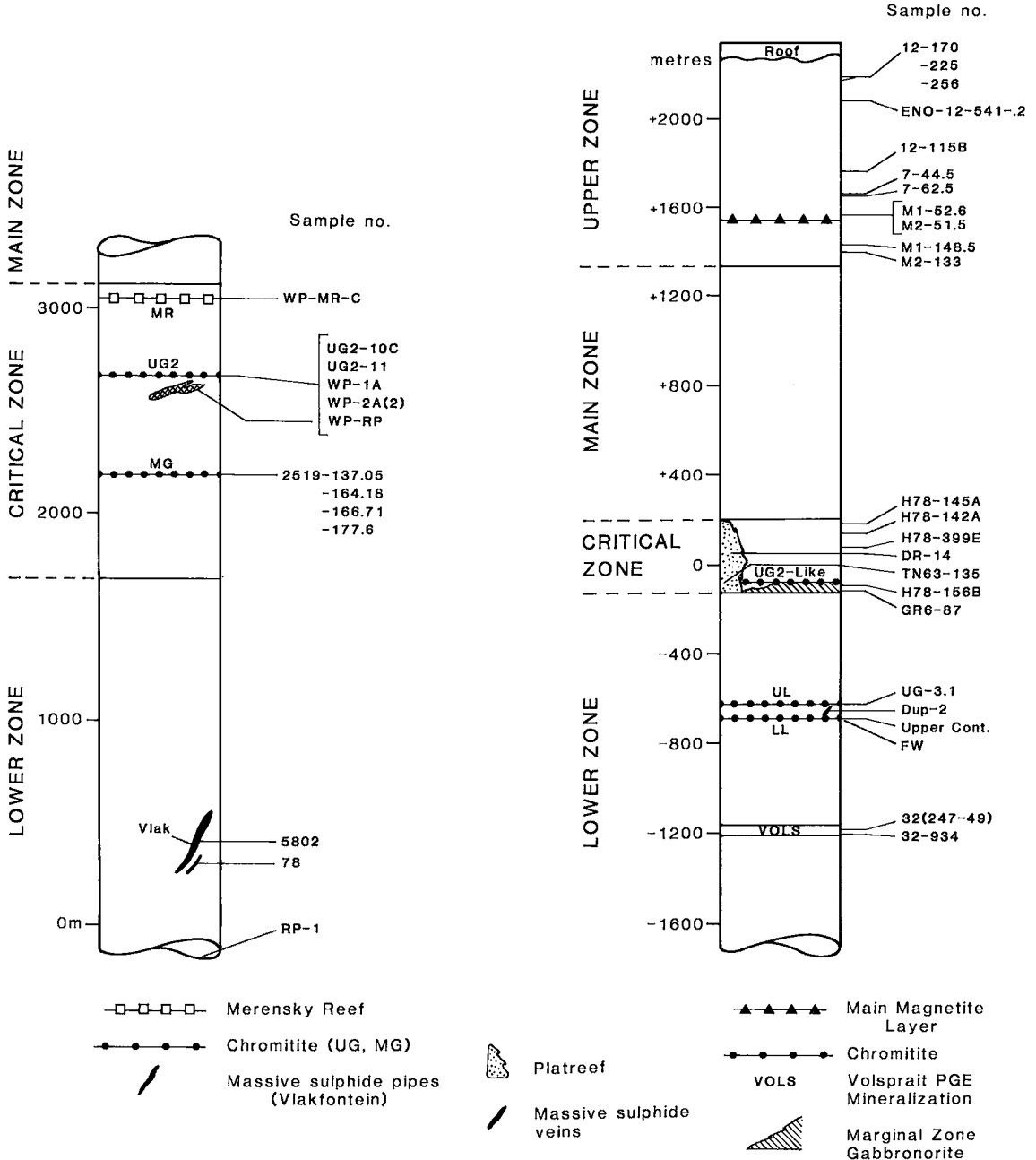


FIG. 1. Sample locations with respect to the simplified Bushveld igneous stratigraphy.

TABLE 1. DESCRIPTION OF SAMPLES.

Location	Sample no	Area	Subzone	Rock Type
Bushveld	12-11588	N		magnetite layer
	12-170	N		olivine diorite
	12-225	N		olivine diorite
	12-2568	N		olivine diorite
	2519-137.05	W	MG-3	pyroxenite
	2519-164.18	W	MG-3	pyroxenite
	2519-166.71	W	MG-3	pyroxenite
	2519-177.6	W	MG-3	pyroxenite
	32(247-249)	N	Volapruit PGE	pyroxenite
	32(934)	N	Volapruit PGE	pyroxenite
	5802	W	Vlakfontein pipe	massive sulfide
	78	W	Vlakfontein pipe	massive sulfide
	AP-1	E	satellite	peridotite
	DR14-174.1-7	N	Platreef	feldspathic pyroxenite
	DR14-35-35.7	N	Platreef	feldspathic pyroxenite
	DUP-2	N		massive sulfide
	END12-541.2	N		anorthosite
	F.W.	N	footwall LG	dunite
	GR6-87	N		gabbro
	H78-142A(1)	N		feldspathic pyroxenite
	H78-142A(2)	N		feldspathic pyroxenite
	H78-1568	N		gabbro
	H78-399E	N		anorthositic norite
	H78-145A	N		gabbro
	LL-2	N	LG	chromitite
	M1-148.85	N	LM	magnetite layer
	M1-52.6	N	footwall MM	pyroxenite
	M2-133	N	LM	magnetite layer
	M2-51.5	N		anorthosite
	M7-191.4	N	LM	magnetite layer
	M7-44.5	N		gabbro
	M7-62.3A	N		anorthosite
	M7-62.3B	N		magnetite
	TN63-135	N		feldspathic peridotite
	UG-3.1	N		dunite
	UG2-10C	W	UG-2	massive sulfide (PGE-rich)
	UG2-11	W	UG-2	massive sulfide (PGE-poor)
	WP-1A	W	UG-2	chromitite
	WP-2A(2)	W	UG-2	chromitite
	WP-MR-X	W	MR	feldspathic pyroxenite
WP-RP	W	below UG-2	Fe-rich pegmatoid	
Upper cont.	N	LG	chromitite	
Cuthbert	C-5(1)		gabbro	
	C-5(2)		gabbro	
Goodwin Lk.	70-13-523(1)	MS	norite	
	70-5-152B	MS	norite	
	70-5-252	MS	massive sulfide	
	70-6-234	MS	massive sulfide	
	71-5B-234	MM	massive sulfide	
Mechanic Muskox	H8B87-94		feldspathic peridotite	
	H8B87-116		massive sulfide	
	H8B87-118-1		massive sulfide	
	H8B87-118.2		massive sulfide	
	H8B87-120		massive sulfide	
	H8B87-120		massive sulfide	
	H8B87-121X		massive sulfide	
	H8B87-122		massive sulfide	
	RES19-306.9		massive sulfide	
	RES21-606.5		massive sulfide	
Namew Lk.	RES21-606.5B		massive sulfide	
	RES25-660		peridotite	
	RES27-606.5		massive sulfide	
	RES29-671.5		massive sulfide	
	RES40-840		remobilized massive sulfide	
	RES40-857.3		remobilized massive sulfide	
	RES49-1115		peridotite	
	RES87-608		massive sulfide	
	RES87-608(1)		massive sulfide	
	RES87-608(2)		massive sulfide	
Rottenstone	HDB84-11		peridotite	
	HDB84-12		metasediment	
	HDB84-13A		pyroxenite	
	HDB84-15A(1)		pyroxenite	
	HDB84-18		pyroxenite	
	HDB84-20		peridotite	
	HDB84-20(2)		peridotite	
St. Stephen	HDB84-21		peridotite	
	HDB84-23B		peridotite	
	B-58-227	HC	semimassive sulfide	
	RF-150-2	RF	semimassive sulfide	
	RF-150-3	RF	massive sulfide	
Wellgreen	RF-150-3(1)	RF	massive sulfide	
	HDB87-24		massive sulfide	
	HDB87-29		massive sulfide	
	HDB87-29(1)		massive sulfide	
	HDB87-29(2)		massive sulfide	
	HDB87-34(1)		massive sulfide	
	HDB87-34(2)		massive sulfide	

Bushveld: E, eastern; N, northern; W, Western; LG, lower chromitite; LM, lower magnetite layer; MG-3, main chromitite; MM, main magnetite layer; Goodwin Lakes: MS, Maliseet south; MM, Maliseet Mountain. St. Stephen: HC, Hall-Carroll; RF, Rogers Farm.

GEOLOGICAL BACKGROUND AND SAMPLES SELECTED

The Bushveld Complex

The Bushveld Complex of South Africa is the largest layered mafic-ultramafic massif in the world. The rocks of the complex crop out in three crudely arcuate areas commonly referred to as the western (Rustenburg), eastern, and northern (Potgietersrus) compartments (Von Gruenewaldt 1979). The layered rocks in the western and the northern compartments have been subdivided into the Lower, Critical, Main and Upper zones. The world's largest known reserves of PGE occur in the Merensky Reef and the UG-2 chromitite of the Critical Zone. The Critical Zone also hosts significant reserves of chromite and low-grade Ni-Cu sulfides. The Upper Zone of the complex hosts Fe-Ti-V deposits. The Lower Zone of the northern limb also contains significant PGE mineralization (Hulbert & Von Gruenewaldt 1982). Thirty-two sulfide-bearing samples collected from the Lower, Critical, and Upper zones of the western and the northern compartments of the Bushveld Complex (Fig. 1, Table 1) were selected for micro-PIXE studies.

The Rottenstone deposit

The Rottenstone Ni-Cu-PGE sulfide deposit occurs in a small ultramafic sill in the Rottenstone lithostructural domain of the Churchill Province in northern Saskatchewan (Hulbert & Paktunc 1989). Mineralization occurs in the form of disseminated, interstitial, and massive sulfides in both harzburgite and orthopyroxenite (Hulbert & Paktunc 1989). Nine samples representing these types were studied (Table 1).

The Namew Lake deposit

The Namew Lake Ni-Cu-PGE sulfide deposit is hosted by a pipe-like ultramafic body (Pickell 1988) that intrudes the Aphebian Flin Flon greenstone belt in central Manitoba. Eleven samples of massive sulfide and peridotite with interstitial sulfide were studied (Table 1).

The Muskox intrusion

The Muskox intrusion is a large body of layered mafic-ultramafic rocks, located in the Bear structural province of the Canadian Shield, in the Northwest Territories. In addition to minor disseminated sulfides in the layered rocks, there are massive to semimassive concentrations of sulfide along the footwall contacts of the intrusion (Hulbert *et al.* 1988). Five samples of massive sulfide, containing cubanite, chalcopyrite and pyrrhotite, were selected for this study from a trench near the southern end of MacGregor Lake.

data obtained will provide a better understanding of the petrological aspects of sulfides in magmatic systems.

TABLE 2. CONCENTRATIONS OF SELECTED TRACE ELEMENTS IN PENTLANDITE AS DETERMINED BY PROTON MICROPROBE

Sample no	C	Co	Ga	Se	Ru	Rh	Pd	Ag	Sn	Sb	Te	Ir	Bi
RUSKVELD													
2519-137.05	10	69668 ±1265	-	10 ±3	-	-	-	-	-	-	20 ± 6	-	-
2519-164-18	5	96982 ±1553	-	9 ±4	-	-	-	-	-	-	-	-	-
2519-166.71	10	89721 ±1349	-	13 ±3	-	-	-	8 ±3	-	-	-	-	-
2519-177.6	5	88316 ±1572	-	13 ±4	-	-	-	-	-	-	-	-	-
32(247-249)	3	23420 ±1682	-	102 ±6	11 ±4	27 ±5	195 ± 9	-	-	23 ±10	-	-	-
32(247-249)	5	24300 ±1476	20 ± 9	79 ±5	-	41 ±5	191 ± 7	-	-	-	-	-	-
32(247-249)	10	23919 ±1348	-	71 ±4	-	-	150 ± 5	-	-	-	-	-	-
32(934)	5	15768 ±1633	-	68 ±5	-	-	42 ± 5	-	-	-	-	-	28 ±14
5802	10	56155 ±1258	-	27 ±3	-	-	-	-	-	-	-	-	-
5802	5	54301 ±1472	-	35 ±4	-	-	8 ± 4	-	-	-	-	-	-
78	5	20436 ±1596	-	44 ±5	-	-	-	-	-	-	-	-	-
AP-1	5	5591 ±1835	17 ± 9	19 ±4	-	-	-	-	15 ±6	-	-	-	-
DR14-174.1-7	5	8916 ±1408	33 ± 9	143 ±5	-	-	101 ± 6	-	-	-	-	-	-
DR14-35-35.7	5	6759 ±1605	-	264 ±6	9 ±3	-	440 ±10	57 ±5	-	-	-	-	-
DR14-35-35.7	5	2147 ±1596	-	272 ±6	12 ±3	-	371 ±10	60 ±6	-	-	-	-	-
F.W.	5	13228 ±1281	-	199 ±6	14 ±4	-	-	-	-	-	51 ±10	73 ±29	-
F.W.	5	13824 ±1292	-	206 ±6	9 ±4	-	8 ± 4	-	-	19 ± 7	28 ±10	69 ±30	-
F.W.	3	12822 ±1444	-	221 ±8	22 ±4	-	50 ± 8	-	-	22 ± 9	-	-	-
H-78-142A(1)	5	10245 ±1347	26 ± 9	158 ±5	-	-	-	-	-	15 ± 7	-	-	-
H-78-142A(2)	5	15663 ±1397	-	123 ±5	-	-	-	-	-	-	-	-	-
H-78-142A(2)	10	14912 ±1199	-	139 ±4	-	-	7 ± 3	-	-	-	-	-	-
H-78-1568	5	26965 ±1501	-	54 ±5	-	-	-	-	-	-	30 ± 8	-	-
H-78-399E	5	7139 ±1395	-	75 ±5	9 ±3	-	115 ± 6	-	-	-	-	-	-
LL-2	5	7061 ±1485	-	95 ±5	-	-	-	-	-	-	-	-	-
M2-51.5	5	13423 ±1396	22 ± 9	90 ±5	13 ±3	-	239 ± 7	18 ±4	-	-	-	-	-
M2-51.5	5	11512 ±1338	-	63 ±5	8 ±3	-	211 ± 7	9 ±4	-	-	-	-	-
M7-62.3A	5	76075 ±1527	-	428 ±7	-	-	-	-	-	-	-	-	-
M7-62.3A	10	72957 ±1285	-	182 ±4	-	6 ±2	-	-	-	-	37 ± 7	-	-
TN63-135	5	21371 ±1461	-	37 ±5	-	-	52 ± 5	-	-	-	-	-	-
TN63-135	5	20504 ±1434	-	101 ±5	-	-	48 ± 5	-	18 ±5	-	-	-	-
UG-3.1	5	23316 ±1403	18 ± 9	91 ±5	-	-	-	-	-	-	92 ±12	-	-
UG-3.1	3	23152 ±1596	-	82 ±6	-	-	-	-	-	-	-	-	-
UG-3.1	10	22322 ±1222	-	77 ±3	-	-	6 ± 3	-	-	-	100 ± 9	-	-
UG2-10C	10	34388 ±1267	-	127 ±4	-	-	13 ± 3	-	-	-	-	-	-
UG2-10C	5	35887 ±1486	27 ± 9	135 ±5	-	-	-	-	-	33 ± 6	-	-	-
UG2-11	5	15326 ±1518	-	85 ±5	8 ±4	12 ±4	264 ± 8	-	-	-	-	-	-
WP-1A	5	32656 ±1526	-	202 ±6	-	-	292 ± 8	-	-	14 ± 7	-	-	-
WP-2A(2)	5	29794 ±1545	-	87 ±5	-	-	56 ± 5	14 ±5	-	-	-	-	-
WP-MR-X	5	9268 ±1444	-	205 ±6	44 ±4	36 ±4	566 ±11	-	-	-	-	-	-
WP-MR-X	5	8677 ±1435	18 ± 9	314 ±6	61 ±5	30 ±4	514 ±11	-	-	-	-	-	-
upper cont.	3	8990 ±1732	-	109 ±7	-	-	-	-	-	-	-	-	-
CUTHBERT													
C-3(2)	1	4088 ± 446	-	187 ±3	-	-	16 ± 2	26 ±3	-	-	-	-	-
GOODWIN LAKE													
70-5-152B(1)	5	74832 ±1583	-	34 ±5	-	-	-	-	-	-	34 ± 9	-	-
70-5-252(1)	10	65231 ±1334	-	33 ±3	5 ±2	-	-	-	-	-	-	-	-
70-6-234(1)	10	55028 ±1337	-	37 ±3	-	-	-	-	-	-	-	-	-
70-13-523	5	53098 ±1512	-	29 ±5	-	-	-	-	-	-	-	-	-
MEANEY LAKE													
RES19-306.9	10	1509 ± 696	14 ± 7	948 ±7	-	-	-	36 ±3	-	-	-	-	188 ±17
RES25-660	10	3145 ±1206	-	199 ±4	-	-	16 ± 3	8 ±3	-	-	-	-	-
RES27-606.5	10	2682 ±1184	-	148 ±4	-	-	-	-	-	22 ± 4	-	-	-
RES29-671.5	5	2027 ±1202	22 ± 9	177 ±6	-	-	-	33 ±5	-	-	-	-	100 ±17
RES29-671.5	5	-	-	141 ±5	-	-	10 ± 4	17 ±5	-	-	22 ± 8	-	-
RES40-840	10	1938 ±1085	-	171 ±4	-	-	7 ± 3	89 ±4	-	-	25 ± 6	-	87 ±13
RES40-840	5	1787 ±1240	-	176 ±6	-	-	-	92 ±6	16 ±7	-	-	-	99 ±17
RES40-857.3	5	5467 ±1234	-	312 ±6	-	-	-	279 ±9	-	-	29 ± 9	-	51 ±17
RES40-857.3	5	3802 ±1279	-	208 ±6	-	8 ±3	-	32 ±4	20 ±5	-	-	-	-
RES49-1115	5	3529 ±1390	-	183 ±6	-	7 ±3	-	-	-	-	-	-	-
RES87-608(1)	10	3363 ±1140	-	147 ±4	-	5 ±2	8 ± 3	-	-	-	-	-	-
RES87-608(2)	5	2909 ±1418	-	148 ±6	-	-	8 ± 4	-	-	-	24 ± 8	-	-
ROTTERSTONE													
HD884-11	5	10790 ±1375	-	137 ±5	-	-	10 ± 4	-	-	-	78 ±12	-	-
HD884-13A	10	10898 ±1201	-	103 ±4	-	-	-	7 ±3	-	-	-	-	-
HD884-15A(1)	10	11440 ±1288	-	113 ±4	-	-	8 ± 3	8 ±3	-	-	-	-	-
HD884-18	10	10508 ±1243	-	112 ±4	-	-	-	-	10 ±4	-	-	-	-
HD884-20(2)	5	9570 ±1283	19 ±11	123 ±5	-	-	-	20 ±4	-	-	-	-	-
HD884-20(2)	5	11746 ±1356	21 ±10	109 ±5	7 ±3	-	-	17 ±4	-	-	-	-	-
HD884-21	10	11334 ±1231	-	123 ±4	-	-	17 ± 3	-	-	15 ± 5	-	-	-
HD884-23B	10	10886 ±1172	-	139 ±4	-	-	-	19 ±3	12 ±4	-	-	-	-
ST. STEPHEN													
RF-150-2	10	83887 ±1313	-	26 ±3	-	-	-	11 ±3	-	-	-	-	-
WELLSGREEN													
HD887-29(1)	5	27118 ±1467	-	129 ±5	-	-	13 ± 4	-	14 ±5	-	-	-	-
HD887-34(1)	1	21589 ±1103	-	86 ±3	-	-	17 ± 3	-	-	10 ± 5	-	-	-
HD887-34(2)	5	36232 ±1476	-	126 ±5	-	-	-	-	-	-	-	-	-

Numbers next to concentration values represent analytical error, in ppm. C, proton charge in microcoulombs.
-, not detected.

The St. Stephen intrusion

The St. Stephen intrusion, located in southwestern New Brunswick, is composed of tholeiitic mafic-ultramafic rocks of Devonian age. The intrusion contains numerous zones of significant Ni-Cu sulfide mineralization (Paktunc 1989a). Three semimassive to massive sulfide samples were studied (Table 1).

The Goodwin Lake intrusion

The Goodwin Lake intrusion, located in northern

New Brunswick, is a small body of mafic-ultramafic rocks (Paktunc 1988). The intrusion and associated Ni-Cu sulfide mineralization are somewhat similar to those in the St. Stephen occurrence (Paktunc 1990). Five samples of semimassive, massive and interstitial sulfides were studied (Table 1).

The Mechanic intrusion

The Mechanic intrusion is a lenticular, layered mafic-ultramafic body that occurs in a late Precambrian terrane in southern New Brunswick (Paktunc

TABLE 3. CONCENTRATIONS OF SELECTED TRACE ELEMENTS IN CHALCOPYRITE AS DETERMINED BY PROTON MICROPROBE

Sample no	C	Ni	Zn	Ge	Se	Pd	Ag	Cd	In	Sn	Te
BUSHVELD											
DR14-174.1-7	5	376 ±109	398 ± 43	-	98 ±5	-	29 ±5	-	-	-	25 ± 9
GR6-87	5	-	417 ± 41	20 ± 6	55 ±5	-	11 ±4	-	-	16 ± 6	-
H78-142A(1)	5	-	161 ± 43	-	112 ±5	-	21 ±5	-	-	-	-
H78-142A(2)	5	-	746 ± 47	-	148 ±6	-	-	-	-	-	-
M1-148.85	5	-	1399 ± 52	-	141 ±5	-	10 ±4	-	15 ±5	-	27 ±10
M2-133	5	-	300 ± 43	-	206 ±6	-	42 ±5	-	-	-	-
M2-51.5	5	208 ±114	377 ± 43	-	155 ±5	-	38 ±5	14 ±5	-	-	-
M7-191.4	15	19314 ±132	451 ± 25	12 ± 4	237 ±3	-	93 ±4	14 ±3	-	-	15 ± 7
M7-62.3A	5	-	282 ± 43	-	208 ±6	-	75 ±6	-	14 ±7	-	-
TN63-135	5	-	260 ± 43	-	75 ±5	-	13 ±4	-	-	-	-
WP-1A	5	364 ±112	313 ± 41	29 ± 7	190 ±6	-	-	-	-	-	-
WP-MR-X	5	-	607 ± 45	-	110 ±5	-	-	-	-	-	-
CUTHBERT											
C-5	5	-	4283 ±124	-	175 ±8	-	-	-	-	-	-
C-5(2)	5	-	258 ± 56	18 ± 9	196 ±6	-	-	-	-	12 ± 5	-
GOODWIN LAKE											
70-5-252	1	-	-	-	41 ±5	-	-	-	-	-	-
70-5-252(2)	10	-	-	-	29 ±5	-	-	-	10 ±4	-	-
70-6-234(2)	10	-	-	-	42 ±5	-	13 ±4	13 ±4	12 ±4	16 ± 5	18 ± 7
71-56-234	1	-	-	-	34 ±5	-	-	17 ±4	-	-	20 ± 7
71-56-234(2)	10	-	-	-	35 ±5	-	-	19 ±4	-	-	25 ± 7
74-6-234	1	-	-	-	44 ±5	-	14 ±4	13 ±4	12 ±4	16 ± 5	-
MECHANIC											
ME87-54	10	334 ± 86	232 ± 29	15 ± 5	244 ±4	-	111 ±5	-	-	-	-
MUSKOK											
HDB87-116	1	-	209 ± 54	21 ± 8	120 ±5	-	11 ±3	-	-	-	-
HDB87-118.2	1	-	273 ± 58	-	-	-	-	-	-	-	44 ±19
HDB87-120	5	256 ±111	826 ± 48	-	375 ±7	-	-	-	-	30 ± 8	-
HDB87-121X	5	333 ±113	194 ± 42	-	295 ±6	-	-	-	23 ±6	46 ± 9	-
HDB87-121X	5	617 ±116	166 ± 41	20 ± 7	293 ±6	-	13 ±4	-	13 ±4	70 ± 8	-
HDB87-121X	10	393 ± 90	221 ± 30	18 ± 5	285 ±4	-	6 ±3	-	21 ±4	54 ± 6	-
HDB87-122	5	4501 ±149	161 ± 45	18 ± 7	287 ±6	-	-	-	-	-	23 ±11
HDB87-122	10	10054 ±133	230 ± 32	17 ± 5	313 ±5	-	-	26 ±4	-	-	40 ± 8
NAMEW LAKE											
RES21-606.5	5	-	863 ±605	-	84 ±7	-	-	25 ±5	-	-	-
RES25-660	5	-	-	-	116 ±8	-	11 ±4	13 ±5	-	-	-
RES25-660	5	-	239 ± 82	-	104 ±7	-	16 ±5	-	-	-	-
RES27-606.5	5	-	810 ±556	-	81 ±7	-	-	24 ±5	-	-	-
RES29-671.5	5	1148 ±441	-	-	97 ±8	-	-	-	-	-	-
RES29-671.5	5	1017 ±387	-	-	97 ±7	-	-	-	-	-	-
RES40-857.3	5	-	-	-	230 ±8	-	59 ±6	-	-	-	-
RES40-857.3	5	-	-	-	239 ±8	-	59 ±6	-	-	-	-
RES49-1115	5	-	916 ± 90	-	96 ±7	10 ±4	-	-	-	-	-
RES49-1115	5	-	845 ±560	-	95 ±7	12 ±4	35 ±6	13 ±6	-	-	-
ROTTENSTONE											
HDB84-11	5	2790 ±472	-	-	143 ±8	-	-	-	-	-	26 ± 9
HDB84-11	5	3186 ±537	-	-	151 ±8	-	-	-	-	-	-
HDB84-12	5	3360 ±472	-	-	92 ±7	-	16 ±5	-	-	-	-
HDB84-12	5	-	679 ± 78	45 ±12	91 ±7	-	83 ±7	-	-	42 ± 9	-
HDB84-15A	5	1741 ±466	-	-	93 ±7	-	40 ±6	15 ±5	-	-	-
HDB84-15A(1)	5	1528 ±409	-	-	89 ±7	-	44 ±6	13 ±5	-	-	-
HDB84-20	5	-	-	-	10 ±4	-	-	-	-	-	-
ST. STEPHEN											
B-58-227	10	-	-	27 ± 8	32 ±5	-	39 ±4	18 ±4	-	-	-
B-58-227	5	-	737 ±112	61 ±17	75 ±6	-	77 ±7	36 ±8	-	-	-
RF-150-3	1	-	-	-	47 ±5	-	-	31 ±4	-	36 ± 6	-
RF-150-3(1)	10	-	-	-	46 ±5	-	-	31 ±4	-	36 ± 6	-
WELLGREEN											
HDB87-24	5	-	472 ± 78	-	125 ±8	-	-	-	-	-	-
HDB87-29	5	1424 ±448	152 ± 79	-	37 ±9	142 ±8	-	19 ±4	-	-	-

Numbers next to concentration values represent analytical error, in ppm. C, proton charge in microcoulomb. -, not detected.

1989b). *PGE* mineralization occurs in several disseminated sulfide zones at different stratigraphic levels. Only one sample from the lowestmost *PGE*-mineralized zone was studied (Table 1).

The Wellgreen deposit

The Wellgreen Ni-Cu-*PGE* deposit occurs in a mafic-ultramafic sill of Triassic age in southwestern Yukon (Hulbert *et al.* 1988). Massive and disseminated sulfides occur both within the sill and foot-wall sediments. Three massive sulfide samples were studied (Table 1).

The Cuthbert Lake dikes

The Cuthbert Lake dikes form part of the Mol-

son dike swarm that intrudes rocks of the Superior Province in north-central Manitoba (Paktunc 1987). Minor amounts of magmatic sulfides are present in the dikes. Although no known Ni-Cu-*PGE* mineralization exists in association with the dikes, several platinum-group minerals (*PGM*), such as merenskyite and irarsite, have been identified in a mafic dike (Paktunc, unpubl. data). One gabbroic sample containing blebby sulfides that host the *PGM* was studied (Table 1).

ANALYTICAL TECHNIQUES

The analyses were carried out with the Guelph University proton microprobe. Analytical conditions were: beam current, 7.6 to 17.3 nA at 3 MeV; beam

TABLE 4. CONCENTRATIONS OF SELECTED TRACE ELEMENTS IN PYRRHOTITE AS DETERMINED BY PROTON MICROPROBE

Sample no	C	Ni	Se	Cd	In	Sb	Te	Os	Ir	Bi
BUSHVELD										
12-1158B	10	1470 ±37	62 ±2	8 ±3	-	-	-	-	-	-
12-170	5	132 ±38	66 ±3	-	-	-	-	-	-	-
12-225	5	141 ±53	110 ±4	-	-	-	-	-	-	-
12-256B	10	70 ±28	62 ±2	-	-	-	-	-	-	-
2519-137.05	5	4508 ±59	11 ±3	-	-	21 ±6	-	-	-	-
2519-164.18	5	1859 ±50	10 ±3	12 ±4	-	-	-	-	-	-
2519-166.71	5	1527 ±47	10 ±3	-	-	-	-	-	-	-
32(247-249)	10	193 ±28	79 ±2	-	-	-	-	-	-	16 ±7
32(247-249)	5	4391 ±59	71 ±3	-	-	-	-	-	-	-
32(934)	5	-	45 ±3	-	-	-	29 ±8	-	-	-
7B	5	-	42 ±3	-	-	-	-	-	-	-
DR14-174.1-7	5	5321 ±57	185 ±4	-	-	-	-	-	-	-
END12-541.2	5	112 ±44	53 ±3	-	-	-	-	-	-	-
H-78-142A(2)	5	10417 ±71	154 ±4	-	11 ±4	21 ±6	-	-	-	-
H-78-399E	5	4999 ±60	130 ±4	-	-	-	-	-	-	-
M1-148.85	5	4137 ±56	145 ±4	10 ±4	-	-	14 ±8	-	28 ±14	-
M1-52.6	5	2522 ±51	159 ±4	-	7 ±4	-	-	36 ±16	32 ±14	-
M2-51.5	5	5934 ±62	147 ±4	-	-	-	-	-	-	-
M7-191.4	5	4412 ±56	162 ±4	-	-	16 ±7	-	-	-	19 ±10
M7-44.5	5	2997 ±51	172 ±4	-	11 ±4	12 ±5	-	-	-	-
M7-62.3A	5	4456 ±58	181 ±4	-	-	-	-	-	-	-
M7-62.3B	10	4665 ±44	169 ±3	-	-	-	-	-	-	-
M7-62.3B	5	4669 ±59	153 ±4	-	-	-	-	-	-	-
TN63-135	5	3401 ±55	57 ±3	-	-	-	-	-	-	-
UG2-10C	5	3280 ±54	118 ±4	-	11 ±4	-	-	-	-	-
UG2-10C	10	3740 ±42	130 ±2	-	-	-	17 ±6	-	-	-
UG2-11	5	6307 ±64	86 ±3	-	-	-	-	-	-	-
WP-1A	5	-	212 ±4	-	-	-	-	-	-	-
WP-MR-X	5	4216 ±57	176 ±4	-	-	18 ±6	-	-	-	-
WP-RP	5	-	104 ±3	-	-	-	20 ±9	-	-	-
upper cont.	5	64 ±41	85 ±3	-	-	-	-	-	-	-
CUTHBERT										
C-5(1)	1	3265 ±33	159 ±2	-	5 ±2	-	-	-	-	-
GOODWIN LAKE										
70-13-532(1)	5	3196 ±60	41 ±3	-	-	-	-	-	-	-
70-5-152(2)	1	3794 ±49	32 ±2	-	-	-	-	-	-	-
70-5-252(1)	5	4722 ±65	31 ±3	-	-	-	-	-	-	-
70-6-234(1)	1	3463 ±48	40 ±2	-	-	18 ±4	-	-	-	-
71-56-234(2)	1	5025 ±52	35 ±2	-	-	-	-	-	-	-
NAMEW LAKE										
RES21-606.5B	5	5181 ±61	218 ±4	-	-	-	-	-	-	-
RES25-660	5	6792 ±39	295 ±4	13 ±3	-	-	-	-	-	-
RES87-608(2)	1	4335 ±47	182 ±3	-	-	-	-	-	-	-
ROTTENSTONE										
HDB84-12	5	3169 ±56	80 ±3	-	-	-	-	-	-	-
HDB84-13A	1	4752 ±48	126 ±3	-	-	-	19 ±6	-	-	14 ±7
HDB84-15A(1)	5	2377 ±57	131 ±4	-	-	-	-	-	-	-
HDB84-18	5	2768 ±59	118 ±4	12 ±4	-	-	-	-	-	-
HDB84-20(2)	5	1298 ±51	116 ±3	-	-	-	-	-	-	-
HDB84-21	1	2044 ±41	137 ±3	-	13 ±3	-	-	-	-	14 ±7
HDB84-23B	1	2336 ±43	139 ±3	-	-	-	-	-	-	14 ±7
ST. STEPHEN										
B-58-227	5	5055 ±65	47 ±3	-	-	-	24 ±8	-	-	-
RF-150-3	5	3550 ±60	39 ±3	-	-	-	-	-	-	-
WELLGREEN										
HDB87-29(1)	1	4389 ±47	111 ±2	-	-	-	-	-	-	-
HDB87-29(2)	5	6251 ±65	99 ±3	-	-	-	-	-	-	-
HDB87-34(2)	5	4683 ±64	133 ±4	-	-	-	29 ±8	-	-	-

Numbers next to concentration values represent analytical error, in ppm. C, proton charge in microcoulomb. -, not detected.

size, 15 μm . X rays emitted from samples were detected with an Ortec Si(Li) detector. Counting times varied from 4 to 22 minutes. The aluminum absorber used for the analysis of pyrrhotite was 249 μm thick, whereas that used for the analysis of pentlandite and chalcopyrite was 365 μm thick. A synthetic pyrrhotite standard containing 60.93 wt.% Fe, 38.87 wt.% S, 0.09 wt.% Se and 0.11 wt.% Pd was used for calibration. Data reduction was carried out using the computer program GUPIX developed at the University of Guelph (Maxwell *et al.* 1989). Details of calibration and data reduction are given in Campbell *et al.* (1987) and Campbell *et al.* (1990).

Detection limits are matrix-dependent and vary as a function of counting time. Minimum detection-limits (MDL) are expressed as:

$$\text{MDL (ppm)} = (3*s)/(4*\pi*H*Yt*e*T),$$

where s is the standard deviation of the background area in one fwhm (full-width, half-maximum) channel range, H is the standardization value used in conversion of area to concentration, Yt is the theoretical thick-target yield of $K\alpha$ or $L\alpha$ X rays per micro-coulomb of proton charge per unit concentration of the element per steradian in one fwhm

channel range centered about the principal peak of the element, ϵ is relative detector efficiency, and T is transmission of X rays through the aluminum absorber. Only the concentration levels that are above the MDL are given in Tables 2, 3, and 4; therefore, instead of providing individual MDL values for each analysis, statistical errors that are related to the square root of the number of counts in one fwhm region of the peak are given. This provides an independent assessment of the results.

Owing to overlap between the peaks of $PtL\alpha$ and $ZnK\beta$, $PtL\beta$ and $SeK\alpha$, and $PtL\gamma$ and $SeK\beta$, and significant concentrations of Se in all of the main sulfide phases and Zn in chalcopyrite, Pt determinations could not be made with confidence. Detection of Ir and Os in pyrrhotite and chalcopyrite was not possible because of interference caused by the $CuK\beta$ peak.

Inclusion-free areas selected with an optical microscope were further examined by SEM to assess the presence of concealed inclusions of *PGM*. The results presented in the following sections are based on a total of 70 analyses of pentlandite, 52 of chalcopyrite, and 52 of pyrrhotite.

Electron-microprobe analyses were obtained using Cameca-CAMEBAX and Cameca-SX50 microprobes equipped with four wavelength-dispersion spectrometers. The samples were analyzed for Ni, Fe, Co, and S at 20 kV and 30 nA, with a 10-second counting time. Analytical conditions for Pd, Ag and Se analysis were 25 kV and 40 nA, with a 40-second counting time. Minimum detection-limits for Pd, Ag, and Se under these conditions were 200, 150, and 300 ppm, respectively. Comparable results for Pd were obtained by proton- and electron-

TABLE 5. COMPARISON OF ELECTRON- AND PROTON-MICROPROBE DETERMINATIONS

Sample no	n	μ PIXE			EPMA			
		Se	Pd	Ag	n	Se	Pd	Ag
upper con	1	109	-	-	5	-	-	-
F.W	3	209 \pm 9	19 \pm 22	-	5	-	-	-
UG-3-1	3	83 \pm 7	2 \pm 3	-	5	-	-	-
SZ(247)	3	84 \pm 13	179 \pm 20	-	5	-	-	-
SZ(934)	1	68	42	-	5	-	-	-
H78-399	1	75	115	-	5	-	-	-
H78-142A	3	140 \pm 14	2 \pm 3	-	5	-	-	-
DR14-35-3	2	268 \pm 4	406 \pm 35	59 \pm 2	5	-	506 \pm 57	-
WP-1A	1	202	292	-	5	-	342 \pm 110	-
WP-MRX	2	260 \pm 77	540 \pm 37	-	5	-	516 \pm 143	-
HF-62.3a	2	278 \pm 212	-	-	5	-	-	-
UG2-11	1	85	264	-	5	-	346 \pm 116	-
M2-51.5	2	77 \pm 19	225 \pm 20	14 \pm 6	5	-	-	-
RES40-857	2	260 \pm 74	-	155 \pm 174	5	-	-	-

EPMA, electron probe micro-analysis; μ PIXE, proton-induced X-ray emission micro-analysis. Values in ppm. -, not detected.

microprobe analysis (Table 5). Because of the high detection-limit of 300 ppm using $SeK\alpha$, and Ni interference on the $SeL\alpha$ peak, assessment of the Se determinations obtained by proton microprobe cannot be made.

PENTLANDITE

Concentrations of the *PGE*, Co, Ag, Ga, Bi, Sn, Sb, Se and Te were measured in pentlandite. Pd concentrations that exceed the MDL of about 8 ppm were found in the Bushveld, Cuthbert, Namew Lake, Rottenstone and Wellgreen samples (Fig. 2). As much as 566 ppm Pd was detected. Values greater than 200 ppm (MDL for the electron microprobe) are comparable with the electron-microprobe data (Table 5). Pd values from the Merensky Reef pentlandite are consistent with the electron-microprobe data of Cabri & Laflamme (1981). Only pentlandite from Bushveld contains measurable quantities of Rh

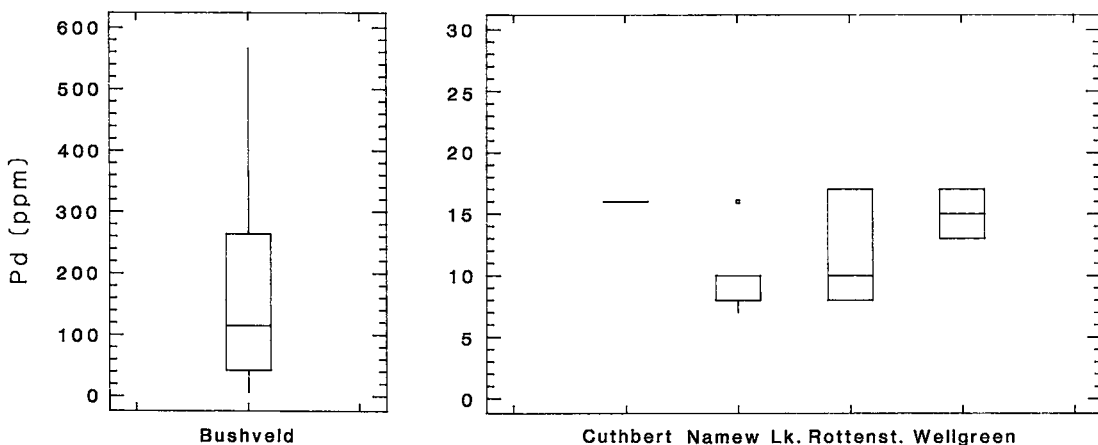


FIG. 2. Box-and-whisker plot illustrating a statistical comparison of the Pd variation in pentlandite. The box covers the middle 50% of the data values, between the lower and upper quartiles, whereas the "whiskers" extend out to the minimum and maximum values. The central line shows the median. Separate points indicate unusual values that occur far from the bulk of the data.

and Ru (12–41 ppm Rh, 9–61 ppm Ru) (Table 2). Rh and Ru may be present in quantities near the MDL of about 5 ppm in the Namew Lake, Goodwin Lake and Rottenstone samples. Ir concentrations of 69 and 73 ppm, obtained from a Bushveld pentlandite, are near the MDL of 60 ppm; therefore, the determinations should be treated with caution. All pentlandite samples analyzed contain measurable quantities of Se (Fig. 3). The highest concentrations

were detected in the Namew Lake pentlandite. Pentlandite from Goodwin Lake and St. Stephen, and some from the Bushveld, contains low levels of Se (*i.e.*, <40 ppm). Se rarely shows significant variation within single grains of pentlandite or among pentlandite grains from the same polished section; with a few exceptions, the variation is within 15% of the concentration. Levels of Co content in pentlandite vary from 0.1 to 9 wt.%. These concentra-

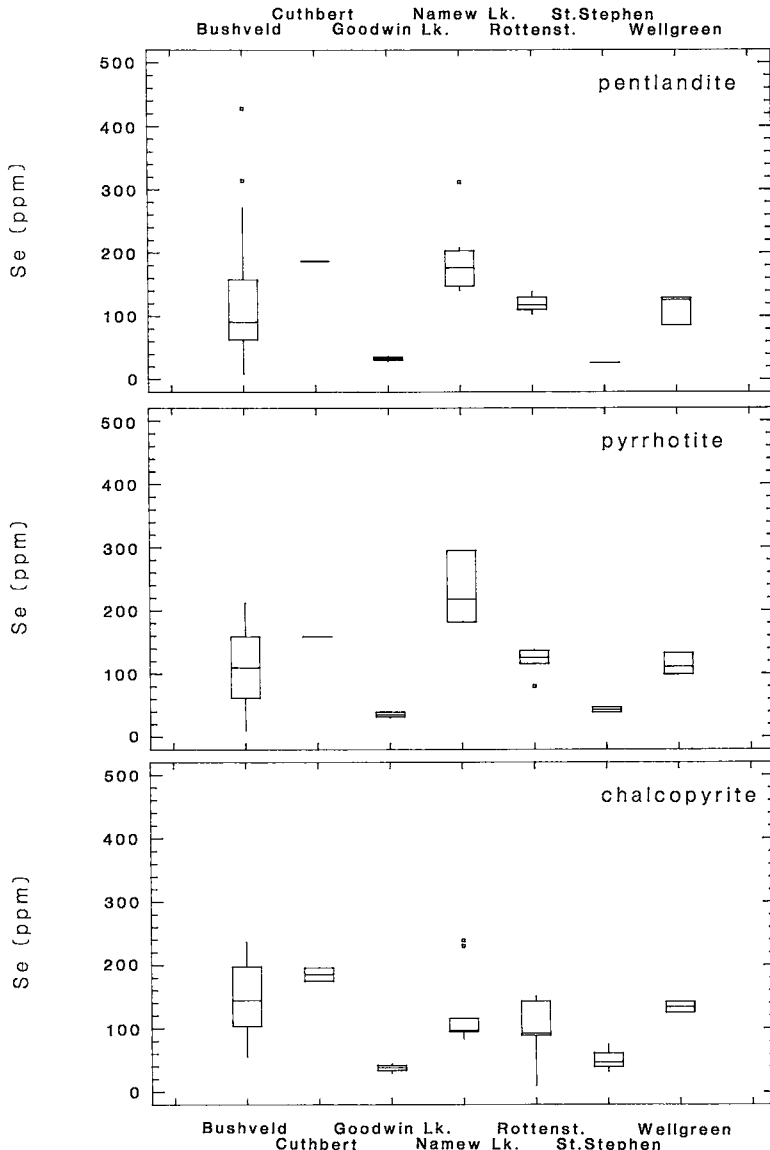


FIG. 3. Box-and-whisker plot comparing the variation of Se concentrations in pentlandite, pyrrhotite and chalcopyrite from the studied occurrences. See Fig. 2 for the explanation of the plot.

tions seem slightly higher than values obtained by electron microprobe (Table 5) because of the overlap between the peaks of Co and Fe. Lower Co contents are found in Namew Lake pentlandite, whereas the highest concentrations characterize pentlandite from the St. Stephen and Goodwin Lake intrusions and the Upper Zone of the Bushveld Complex. Approximately one half of the pentlandite grains contain Ag at detectable levels; Namew Lake pentlandite has the highest concentrations (as much as 90 ppm; Fig. 4). Up to 27 ppm Ga is present in Bushveld, Namew Lake, and Rottenstone pentlandite. Within-grain and within-sample distributions of Ga do not seem to be uniform. One Bushveld and five Namew Lake pentlandite grains contain Bi; concentrations range from 28 to 188 ppm. Sn, Sb, and Te attain levels of 20, 33, and 100 ppm, respectively (Table 2).

CHALCOPYRITE

Elements that are present in measurable quantities in chalcopyrite include Ni, Zn, Ag, Cd, In, Sn, Ge, Se, and Te (Table 3). In general, measurable levels of *PGE* were not detected in chalcopyrite; one chalcopyrite grain from the Namew Lake deposit contains Pd near the MDL of 4 ppm. With the exception of the Goodwin Lake, St. Stephen, and Cuthbert chalcopyrite, all contain significant concentrations of Ni. Concentrations greater than 1 wt. % Ni were encountered in Bushveld and Namew Lake chalcopyrite. Almost all samples analyzed contain Zn and, to a certain extent, Ag. Chalcopyrite from Mechanic was found to contain as much as 111 ppm Ag. Se is present in all samples (Fig. 3). Consistently high concentrations were found in Muskoxy chalcopyrite. Within-grain and within-sample variations of Se appear to be small. As much as 61 ppm Ge is present in some samples.

PYRRHOTITE

Measurable concentrations of Ni, Cd, In, Sb, Bi, Se and Te were found in pyrrhotite (Table 4). Os and Ir concentrations near the detection limits of 35 and 27 ppm, respectively, were observed in two pyrrhotite grains from the Bushveld Complex. Other *PGE* were not detected in any analyzed pyrrhotite. As with pentlandite and chalcopyrite, all pyrrhotite contains detectable concentrations of Se (Fig. 3). Low levels of Te are present in some grains. Only the Bushveld and Goodwin Lake pyrrhotite contains detectable levels of Sb.

DISCUSSION

Pentlandite and chalcopyrite can accommodate a wide variety of elements in their structure, whereas

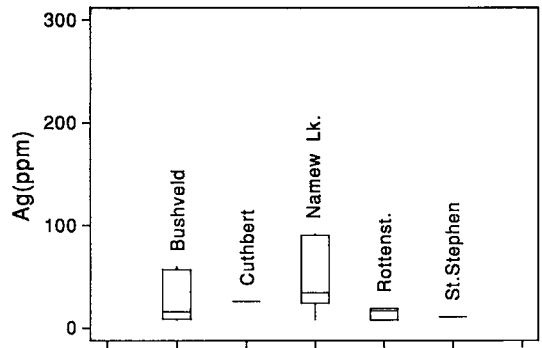


FIG. 4. Box-and-whisker plot illustrating the Ag variation in pentlandite. See Fig. 2 for the explanation of the plot.

the pyrrhotite structure seems to accommodate only a limited number of the trace elements considered.

Platinum-group elements

Among coexisting minerals, pentlandite is the only mineral that accommodates appreciable levels of Pd, Rh and Ru. This is in general agreement with the findings of Cabri *et al.* (1984). Crockett's (1981) data on mineral separates and experimental data of Makovicky *et al.* (1986) also indicate higher concentrations of *PGE* in pentlandite. *PGE*-bearing pentlandite is found in samples from the *PGE*-rich occurrences, such as Bushveld Complex, Namew Lake, Rottenstone and Wellgreen deposits, and the Cuthbert Lake dikes. In the western Bushveld, pentlandite from known platinumiferous horizons such as the UG-2 and the Merensky Reef were found to contain higher levels of *PGE* than that of the non-platinumiferous rocks from the same complex. Although *PGE*-bearing pentlandite is restricted to specific stratigraphic horizons in the western Bushveld, occurrences of *PGE*-bearing pentlandite are more widespread in the northern compartment. There, pentlandite from the basal portion of the Lower Zone, in the basal and upper portions of the Critical Zone, and in the basal portion of the Upper Zone contains Pd in excess of 100 ppm. Among these, pentlandite occurring in a magnetite-rich gabbro near the lower magnetite horizon of the Upper Zone is especially interesting because rocks in this zone are known to be virtually *PGE*-free. The low *PGE* assays for whole-rock samples can be explained by the low modal abundance of pentlandite, which occurs in the form of exsolution blebs.

Pentlandite from *PGE*-rich samples contains less Co than that in *PGE*-poor samples. *PGE*-rich pentlandite from the magnetite-rich gabbro in the basal portion of the Bushveld Upper Zone is an exception. Pentlandite seems to demonstrate a crude positive

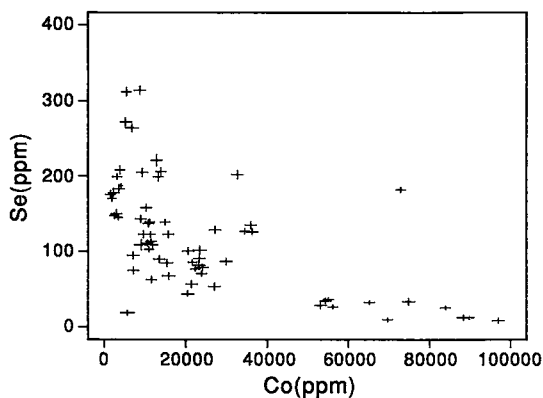


FIG. 5. Relation between Co and Se concentrations in pentlandite.

correlation between Se and *PGE* contents, and a negative correlation between Se and Co contents (Fig. 5). This is in accord with the conclusions of Merkle & Von Gruenewaldt (1986), in that enrichment of cobalt in pentlandite may result from an earlier segregation event involving olivine and an immiscible sulfide melt. According to the experimental results of Distler *et al.* (1977), Pd content of pentlandite increases with an increase in Ni content of pentlandite. Cabri *et al.* (1984) reported no correlation between these elements in samples from the Stillwater Complex. Our data seem to suggest that a crude negative correlation may exist between the Pd content and the Ni/Fe ratio of pentlandite; however, the variation in terms of Ni/Fe ratio is very limited; therefore, this relationship is not conclusive.

All pentlandite enriched in *PGE* is from disseminated sulfide samples. Pentlandite in samples with abundant sulfides contains somewhat lower concentrations of the *PGE*. Pentlandite grains in a massive sulfide sample from the UG-2 that has high whole-rock *PGE* levels contain low *PGE* levels (*i.e.*, Pd < 13 ppm, Ru and Rh below detection limits), whereas a pentlandite grain in a sample of massive sulfide from the UG-2 with a low whole-rock *PGE* level has high *PGE* contents (*i.e.*, 264 ppm Pd, 12 ppm Rh, and 8 ppm Ru). Pentlandite from other *PGE* deposits, such as those from the J-M Reef of the Stillwater Complex and the Lac-des-Iles Complex, in which the sulfides are minor in abundance, also contains *PGE* (Cabri & Laflamme 1981, Todd *et al.* 1982, Cabri *et al.* 1984). Pentlandite from Ni-Cu sulfide deposits and occurrences does not seem to contain appreciable *PGE*. In addition to the examples provided in this study, pentlandite from the Sudbury Ni-Cu sulfide deposits does not contain *PGE* at the MDL levels of the proton microprobe (Cabri *et al.* 1984). Although *PGE* values ranging from 23

to 123 ppm were reported in pentlandite from the Talnakh Ni-Cu sulfide deposit by Genkin *et al.* (1973), their accuracy is questionable in view of the MDL of electron-microprobe analysis. In summary, Ni-Cu sulfide deposits in which *PGE* are recovered as by-products from the Ni-Cu sulfide ore do not seem to contain appreciable amounts of *PGE* in pentlandite, whereas pentlandite grains from the *PGE*-Ni-Cu deposits with disseminated sulfides contain *PGE* at significant levels. The reason for this circumstance is not well understood at present; however, a simple explanation would be the dilution of *PGE* in a larger amount of sulfide matrix in the case of Ni-Cu sulfide deposits. This requires that the initial distribution of *PGE* among immiscible sulfide droplets at liquidus temperatures and during subsequent exsolution of phases from the *mss* be homogeneous. The latter is supported by the experimental studies of Distler *et al.* (1977), which indicate that the partitioning of Pd, Rh and Ru between pentlandite and pyrrhotite is about equal.

There seems to be a relationship between the *PGE* content of pentlandite and the mineralogy of the *PGE*. In the UG-2, the most abundant *PGM* phases are vysotskite, laurite, braggite and cooperite (Peyerl 1982, McLaren & de Villiers 1982, Paktunc *et al.* 1989). The principal *PGM* in the Merensky Reef are braggite, cooperite, Pt-Fe alloys, laurite and sperrylite (Vermaak & Hendriks 1976). In the Platreef, cooperite and braggite dominate the *PGM* assemblage (Gain & Mostert 1982). A similar situation seems to exist at the J-M Reef, in which pentlandite is found to contain high levels of Pd in solid solution (Todd *et al.* 1982, Cabri *et al.* 1984), and the dominant *PGM* include *PGE* sulfides and Pt bismuth-telluride (Todd *et al.* 1982). The Namew Lake deposit is characterized by abundant michenerite and other Pd bismuthotellurides (Paktunc, unpubl. data). The Rottenstone deposit contains michenerite, kotulskite, sperrylite, froodite, hollingworthite, and irarsite (Hulbert & Paktunc 1989, in prep.) The most abundant phases in the Wellgreen deposit are sperrylite, michenerite, moncheite, merenskyite, sudburyite, temagamite and testbiopalladite (Cabri & Laflamme 1989, Paktunc, unpubl. data). The Cuthbert Lake occurrence includes merenskyite, irarsite, and an unnamed Rh-Pt arsenide (Paktunc, unpubl. data). It is interesting to note that the *PGE* sulfides are the most abundant *PGM* species in the occurrences containing pentlandite with high Pd such as UG-2, Merensky Reef, and Platreef. In contrast, pentlandite from the Sudbury (Cabri & Laflamme 1976, Cabri *et al.* 1984), Namew Lake, Rottenstone and Wellgreen deposits, in which the dominant *PGM* are tellurides, bismuthotellurides, and arsenides or sulfarsenides, has somewhat lower concentrations of Pd. It seems that the Te and Bi concentrations in the base-metal sul-

fides play an important role in controlling the exsolution of *PGE* from the base-metal sulfides. In Rottenstone and Namew Lake deposits, for example, the occasional occurrence of Pd-bismuthotellurides along with Ag-tellurides and Bi-tellurides localized near the grain boundaries of the base-metal sulfides and in secondary phases suggests a late magmatic exsolution of *PGE* from the base-metal sulfides (Hulbert & Paktunc, in prep., Paktunc, unpubl. data). Textural studies on the Merensky and Noril'sk ores have led Vermaak & Hendriks (1976) and Genkin & Evstigneeva (1986) to propose that the *PGE* sulfides and alloys are earlier than the *PGE* tellurides, bismuthotellurides and arsenides in the sequence of crystallization. Experimental studies of Distler *et al.* (1977) indicate the importance of S activity in determining whether the *PGE* form discrete *PGM* or remain in solid solution. In summary, the *PGE* that remain in solid solution because of high S activity may exsolve to form *PGE* bismuthotellurides and tellurides at later stages. The availability of Bi and Te in the system would control the extent of the exsolution process and, therefore, the amount of *PGE* remaining in solid solution.

Selenium

Se seems to partition equally among coexisting pentlandite, pyrrhotite and chalcopyrite. On the basis of thirty pairs of pentlandite and pyrrhotite grains, the $(\text{Se})_{\text{pn}}/(\text{Se})_{\text{po}}$ ratio is calculated to be 1.0 ± 0.3 (Fig. 6), the $(\text{Se})_{\text{Cpy}}/(\text{Se})_{\text{pn}}$ ratio, 1.0 ± 0.7 (Fig. 7), and the $(\text{Se})_{\text{Cpy}}/(\text{Se})_{\text{po}}$ ratio, 1.1 ± 0.5 (22 pairs). This result is significant, especially as it bears on the use of the Se/S ratio of bulk-rock samples in petrogenetic studies (*e.g.*, Eckstrand *et al.* 1989). Remobilization of magmatic sulfides, a commonly observed feature of deformed and metamorphosed Ni-Cu sulfide deposits, involves preferential mobilization of chalcopyrite and typically alters the magmatic chemistry of the sulfide assemblage (*e.g.*, Ni/Cu and Pt/Pd ratios). In such cases, Se will be the only element unaffected because of its equal partitioning among the three phases. Bulk Se analysis of remobilized sulfides, therefore, can be used with confidence in petrogenetic studies. In general, sulfides from *PGE*-rich occurrences have a Se/S ratio greater than or within the mantle range (Table 6). Sulfides from the *PGE*-poor Ni-Cu occurrences, such as at St. Stephen and Goodwin Lake, where the sulfur is considered to be mainly of crustal origin (Paktunc 1989a, 1990), display a lower Se/S ratio. Se/S ratios of pentlandite, chalcopyrite and pyrrhotite from the J-M Reef of the Stillwater Complex (Cabri *et al.* 1984) are consistently higher than the mantle range (Table 6). This is also the case for our data on the Merensky Reef sulfides. Sulfides from Sudbury (Cabri *et al.* 1984) display a wide range in

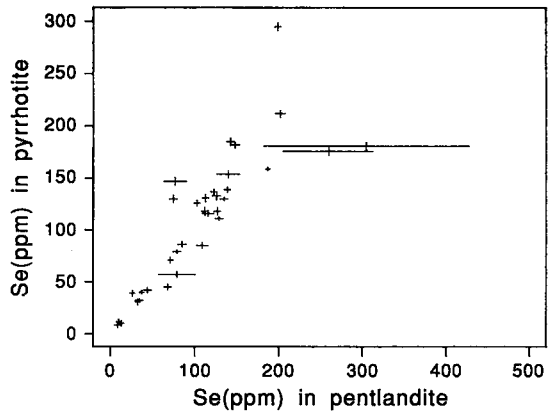


FIG. 6. Distribution of Se between coexisting pentlandite and pyrrhotite.

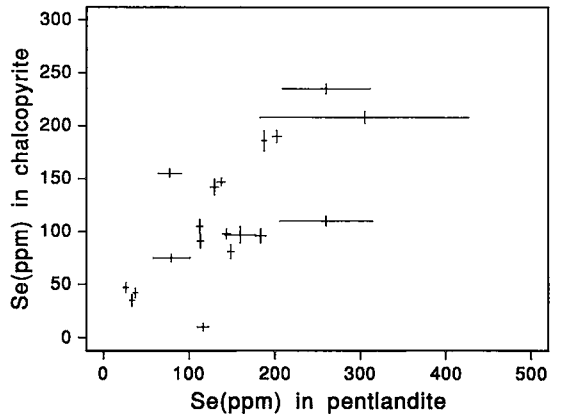


FIG. 7. Distribution of Se between coexisting pentlandite and chalcopyrite.

terms of Se/S value (Table 6), spanning the mantle range. Pentlandite and pyrrhotite in a pyroxenite unit at the MG-3 chromitite layer and in the Vlakfontein pipe of the Bushveld Complex contain very low levels of Se and, consequently, have Se/S ratios much lower than the range of mantle sulfides. These two occurrences are in close proximity to each other; on the basis of their low Se/S ratio and the sulfur isotopic data (Hulbert, unpubl. data), the formation of sulfides in these zones has been attributed to assimilation of sedimentary sulfur from rocks of the Transvaal Basin. Chalcopyrite in the Upper Zone of the northern Bushveld, in general, has a higher Se/S ratio than the mantle range and that in the Critical Zone. Se/S values are generally comparable with those obtained from whole-rock analyses; therefore, all Se reported in whole-rock assays from these

TABLE 6. Se/S RATIOS IN PENTLANDITE, CHALCOPYRITE, AND PYRRHOTITE

Locality	Mineral	Se/S*10 ⁻⁶	n
Upper Zone (N. Bushveld)	chalcopyrite	400-659	6
	pentlandite	191-1297	4
	pyrrhotite	136-464	13
Critical Zone (W. Bushveld)	chalcopyrite	347-612	2
	chalcopyrite	132-471	4
Critical Zone (N. Bushveld)	pentlandite	164-824	10
	pyrrhotite	146-474	4
	pentlandite	206-670	12
Lower zone (N. Bushveld)	pyrrhotite	115-218	4
	pentlandite	621-952	2
Merensky Reef (W. Bushveld)	pyrrhotite	451	2
	pentlandite	258-612	5
UG-2 (W. Bushveld)	pyrrhotite	221-544	5
	pyrrhotite	27-39	4
MG-3 (W. Bushveld)	pyrrhotite	26-28	3
	pentlandite	82-133	3
Vlakfontein pipe (W. Bushveld)	pyrrhotite	108	2
	chalcopyrite	515-576	2
Cuthbert	pentlandite	567	2
	pyrrhotite	408	2
	chalcopyrite	85-129	6
Goodwin Lake	pentlandite	100-112	3
	pyrrhotite	79-105	5
	chalcopyrite	565-718	2
Mechanic	chalcopyrite	353-1103	13
	chalcopyrite	168-915	15
Muskox	pentlandite	88-2933	13
	pyrrhotite	279-756	5
	chalcopyrite	29-444	8
Namew Lake	pentlandite	312-421	8
	pyrrhotite	205-356	7
	chalcopyrite	94-221	4
Rottenstone	pentlandite	79	2
	pyrrhotite	100-121	2
	chalcopyrite	368-418	2
St. Stephen	pentlandite	261-391	3
	pyrrhotite	254-341	3
	chalcopyrite	114-680	3
Wellgreen	pentlandite	154-505	3
	pyrrhotite	254-341	3
	chalcopyrite	794-800	3
Sudbury ¹	pentlandite	980-2041	3
	pyrrhotite	613-877	3
	chalcopyrite	230-350	3
Stillwater (J-M Reef) ¹	pentlandite	980-2041	3
	pyrrhotite	613-877	3
	chalcopyrite	230-350	3
MANTLE ²			

¹ Cabri et al. (1984); ² Ecksstrand et al. (1989).

occurrences can be attributed to solid solution within pentlandite, chalcopyrite and pyrrhotite.

Silver

Ag concentrations as high as 111 ppm in chalcopyrite and 279 ppm in pentlandite have been measured. Almost all chalcopyrite in the Bushveld Complex contains detectable Ag. The presence of Ag in solid solution in chalcopyrite has long been suspected

(e.g., Hawley & Nichol 1961, Thorpe 1967); however, this has not been confirmed by *in situ* analysis until very recently. Harris *et al.* (1984) documented Ag concentrations ranging from 350 to 2630 ppm in chalcopyrite from the Izok Lake massive sulfide deposit, in the Northwest Territories, and from the Hilton Ag-Pb-Zn mine in northwestern Queensland, Australia. In the northern Bushveld, Upper Zone chalcopyrite is enriched in Ag compared to that from the Critical Zone. This enrichment may be due to the evolved nature of the liquid from which the sulfide melt presumably formed, a normal consequence of fractional crystallization. Pentlandite also is known to contain Ag. Argentopentlandite, which occurs in the form of exsolution products in chalcopyrite in a variety of deposits (Scott & Gasparini 1973, Mandziuk & Scott 1977) may contain as much as 15 wt.% Ag. Most of Namew Lake pentlandite contains Ag. In the Bushveld Complex, only PGE-rich pentlandite contains detectable Ag. The distribution of Ag between coexisting pentlandite and chalcopyrite seems to be irregular; Ag may be contained only in pentlandite in some cases, and in others, only in chalcopyrite.

Other elements

Zn appears to partition exclusively into chalcopyrite over pyrrhotite and pentlandite. Variable concentrations above 200 ppm are present in most of the studied chalcopyrite, and as much as 4283 ppm was detected in chalcopyrite from the Cuthbert Lake dikes (Fig. 8). Cabri *et al.* (1984) also reported that Zn is present in variable quantities, from less than 35 ppm (MDL) to 805 ppm in chalcopyrite from Sudbury. Bi and Te do not appear to be preferentially concentrated in any of the three phases. Ge occurs only in chalcopyrite, and Ga seems to prefer the pentlandite structure. Concentrations of Ge and Zn seem correlated in chalcopyrite.

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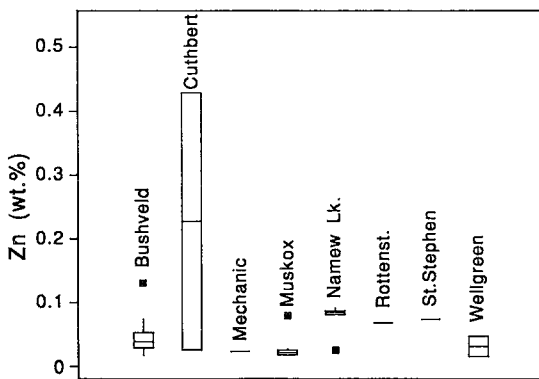


Fig. 8. Box-and-whisker plot for Zn in chalcopyrite. See Fig. 2 for the explanation of the plot.

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