PLATINUM-GROUP MINERALS IN THE RAGLAN Ni–Cu–(PGE) SULFIDE DEPOSIT, CAPE SMITH, QUEBEC, CANADA

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Abstract

Platinum-group minerals (PGM) have been identified in samples from the Katiniq and Zone 2 orebodies, Raglan deposits, Cape Smith, northern Quebec. The most abundant PGM (in area %) is sperrylite, comprising a third of all the grains. Overall, sudburyite and merenskyite make up the majority of the remaining PGM, with the others consisting of moncheite, temagamite, a Pd–Bi telluride, a Pd–Pb–Bi telluride and a Pt–Os–Ru-bearing Rh sulfarsenide, probably hollingworthite. Sperrylite is more abundant at Katiniq, and merenskyite is more abundant in Zone 2. The majority of the PGM are associated with sulfide minerals and are either completely enclosed within sulfides, or at a sulfide–silicate boundary. Platinum-bearing PGM are the predominant PGM associated with pyrrhotite and pentlandite in MSS ores. In addition, the PGM in chalcopyrite-rich ores are commonly Pt-bearing, with Pd-bearing PGM concentrated in secondary veins. A notable proportion of the PGM is associated either with carbonate, 13% by area within Zone 2, or with maucherite (nickel arsenide), 9% by area at Katiniq. The platinum-group elements, especially Pd, have been mobilized during both extensive low-temperature alteration of the ultramafic rocks in the greenschist facies and the shearing that affected these deposits. This fact is demonstrated by the occurrence of sudburyite and, more rarely, sperrylite within carbonate in secondary veins and in shear zones. At Katiniq, sudburyite is associated with maucherite, and Pd occurs in solid solution within the maucherite grains, both minerals likely to have been produced as a result of postmagmatic alteration. The morphology of the PGM has been extensively modified during this low-temperature alteration, with sperrylite crystals losing their euhedral form where parts of the crystal are in contact with altered silicates. These PGM may also have indented outlines where they are cross-cut by needles and laths of actinolite–tremolite. In terms of processing and beneficiation, 20% of the PGM grains may currently be unrecoverable owing to their complete enclosure in gangue minerals. Only 17.5% are fully recoverable as a result of their enclosure within chalcopyrite and pentlandite.

Keywords: platinum-group minerals, Raglan deposits, Katiniq orebody, Cape Smith, Quebec.

Sommaire

Nous avons identifié les minéraux du groupe du platine (MGP) dans des échantillons de minerai provenant des gisements Katiniq et Zone 2, parmi les gisements de Raglan, au Cap Smith, dans le nord du Québec. Le MGP le plus abondant, en termes d'aire, est la sperrylite, qui constitue un tiers des grains. En général, la sudburyite et la merenskyite constituent la majorité des autres grains, et des proportions infimes de monchéite, témagamite, un tellurure de Pd–Bi, un autre de Pd–Pb–Bi, et un sulfarséniure de Rh contenant aussi Pt–Os–Ru, probablement la hollingworthite, forment le reste. La sperrylite est davantage abondante à Katiniq, et la merenskyite est plus abondante à la Zone 2. La majorité des MGP montrent une association avec les minéraux sulfurés et sont soit complètement inclus dans les sulfures ou bien sont situés à l'interface entre sulfure et silicate. Les MGP contenant du platine sont prédominants en association avec la pyrrhotite et la pentlandite dans les minerais massifs (MSS). De plus, les MGP dans les minerais riches en chalcopyrite sont en général aussi platinifères, et les minéraux plutôt palladifères sont concentrés dans les veines secondaires. Une proportion importante des grains de MGP est associée soit au carbonate, 13% selon l'aire dans la Zone 2, soit avec la mauchérite (arséniure de nickel), 9% selon l'aire à Katiniq. Les éléments du groupe du platine, surtout le Pd, ont été remobilisés lors de l'altération intense des roches ultramafiques à faibles températures, sous conditions du faciès schistes verts, et lors du cisaillement qui a affecté ces gisements. Ce fait rend compte de la présence de sudburyite et, moins couramment, de la sperrylite englobés dans le carbonate dans des veines secondaires et dans des zones de cisaillement. A Katiniq, la sudburyite est associée à la mauchérite, et le Pd se trouve en solution solide dans des grains de mauchérite, les deux minéraux probablement produits de l'altération postmagmatique. La morphologie des MGP aurait été fortement modifiée au

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cours de cette altération à basse température; ainsi, les cristaux de sperrylite auraient perdu leur forme idiomorphe où ils étaient en contact avec des silicates produits par l'altération. Ces MGP pourraient aussi avoir un profil indenté où ils sont recoupés par des aiguilles ou des plaquettes d'actinolite–trémolite. En termes de traitement et d'enrichissement des minerais, 20% des grains de MGP seraient présentement non récupérables à cause de leur présence en inclusions dans les minéraux de la gangue. Seulement 17.5% seraient complètement récupérables, étant présents en inclusions dans la chalcopyrite et la pentlandite.

(Traduit par la Rédaction)

Mots-clés: minéraux du groupe du platine, gisements de Raglan, gisement de Katiniq, Cap Smith, Québec.

Introduction

The Raglan Ni–Cu–(PGE) sulfide deposits are located in the New Quebec region of northern Canada, on the Ungava Peninsula, 1540 km north of Rouyn–Noranda. There are 20 distinct mineralized regions found to date, each comprising a number of ore lenses (over 90 in total), all hosted in the Raglan Formation. The orebodies occur over a distance of 55 km, between the Donaldson deposit in the east to Cross Lake in the west (Fig. 1). The two deposits sampled for this study are at Katiniq, where the mine buildings and mill are located and underground mining is in operation, and at the Zone 2 open-pit, which lies approximately 10 km to the west of Katiniq. Dillon-Leitch *et al.* (1986) described the distribution of the PGE as well as of Cu, Ni and associated Au-, Ag-, Te-, Sb-, Bi-, Co- and As-bearing minerals from the Donaldson West deposit in the Raglan area (Fig. 1). They suggested that the PGE grade is related to sulfide content and that remobilization of PGE occurred as the result of regional greenschist-facies metamorphism, where transport of PGE in hydrothermal fluids resulted in the redistribution of Pt and Pd. However, relatively little attention has been paid to PGE mineralogy within the Raglan orebodies.

Falconbridge Ltd. and its subsidiary companies have been exploring these deposits since the late 1950s, but the official mine opening did not take place until the beginning of 1998. At Raglan, Pt and Pd add significantly to the profitability of the mine. A need to optimize Pt and Pd recoveries at Raglan prompted the initiation of mineralogical work to examine the relationship between PGM, ore and gangue minerals. Processing of the Ni–Cu sulfide ore at Raglan is done by conventional methods, using froth flotation and smelting to produce separate concentrates of Ni, Cu and PGE. Pyrrhotite, a large component of the ore, is rejected as gangue.

Our aim in this study is to report on the textures, relative abundance and mode of occurrence of the PGM
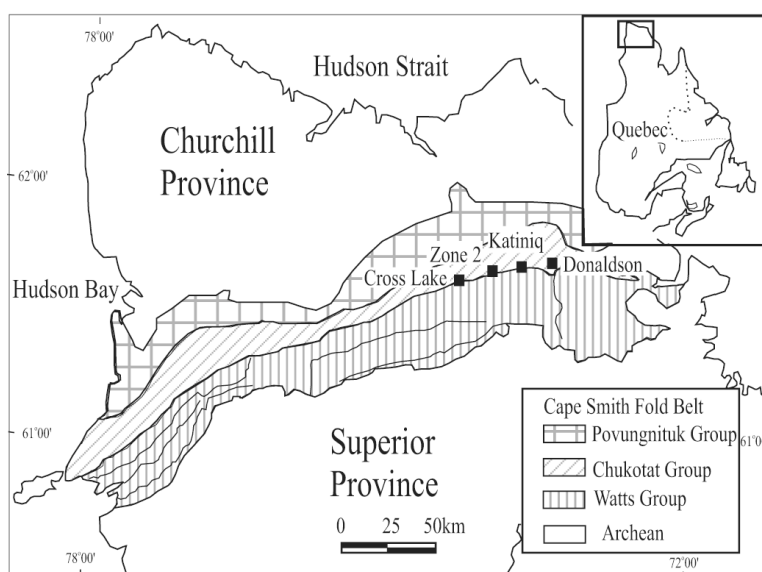

FIG. 1.   Regional geological map of the Cape Smith Fold Belt, showing locations of the sulfide deposits (after Barnes & Picard 1993).

in order to understand both the genesis of the deposit and variations in PGE recovery. The work presented here is confined to only two of the mineralized PGE-bearing Cu- and Ni-rich massive sulfide lenses, Katiniq and Zone 2, and may not necessarily be typical of the Raglan deposits as a whole.

REGIONAL GEOLOGY

The Raglan orebodies are located in the eastern section of the Cape Smith Belt, northern Quebec. This is a Proterozoic thrust belt, preserved as part of the foreland thrust belt to the Ungava Orogen, an arc–continent collisional zone (St-Onge *et al.* 1993). The southern section of the fold belt is composed of the Povungnituk and Chukotat groups (Hynes & Francis 1982) that form parautochthonous sedimentary and volcanic cover units, associated with multiple rifting of the Superior Province (St-Onge *et al*. 2000). The Povungnituk Group consists of a lower unit of continental clastic sediments and a middle unit of intrusive rocks (gabbro, pyroxenite and peridotite sills) and extrusive tholeiitic basalts, and an upper turbidite unit. This sequence is overlain by the Chukotat Group, which comprises intrusive and extrusive rocks of komatiitic to tholeiitic mid-ocean ridge-type basalts (Hynes & Francis 1982, Picard *et al.* 1990).

The deposits lie near the base of the Chukotat Group, in lenses of peridotite of the Raglan Formation at the base of komatiite units (Naldrett 1989). These ultramafic rock-types host the only known mineralization in the Cape Smith Belt (Lesher 1999) and form a series of multiple overlapping channels and flanking levées that are considered to be extrusive in origin (Lesher *et al*. 1999). The entire Cape Smith sequence has been interpreted as representing the transition from initial rifting (lower Povungnituk Group) and continental basalt volcanism (upper Povungnituk Group), to the opening of an ocean basin (Chukotat Group) (Francis *et al*. 1981, 1983, Hynes & Francis 1982, Picard *et al*. 1990). The rocks of this area are metamorphosed to the low to middle greenschist facies (Barnes *et al*. 1982).

THE NI–CU–(PGE) SULFIDE DEPOSITS

The orebodies form lenses composed of massive and disseminated sulfide, created as a result of magmatic segregation occurring in multiple internal horizons, in mesocumulate peridotite, olivine oikocrystic pyroxenite and pyroxenite (Lesher & Charland 1999). The undeformed massive ores display adcumulate textures with equant crystal shapes. The disseminated and net-textured ores contain undeformed replaced silicate crystals surrounded by and isolated from each other by sulfide minerals. Ores that are less sulfide-rich contain isolated grains of sulfide in interstitial positions. The primary igneous features have been variably affected by

shearing. Deformed ores have strikingly different textures displaying aligned intergrowths of sulfide and actinolite–tremolite laths and needles with patches of chlorite and serpentine.

The Katiniq orebody

The Katiniq orebody comprises a number of separate ore zones, the majority of which lie in footwall embayments, at the base of a komatiitic flow. Massive ore grades upward into net-textured and disseminated ore. Typically, the main basal massive sulfide section is made up predominantly of pyrrhotite and pentlandite, with some chalcopyrite, magnetite, carbonate, and minor PGM. In addition, but less commonly, massive sulfides also occur at the base of flows above the basal flow. Massive sulfide horizons typically vary in thickness between 30 cm and 10 m and consistently comprise of over 70% sulfide.

The overlying net-textured ore, which is also found as isolated patches in peridotite, typically comprises 40–70% sulfide (pyrrhotite, pentlandite, chalcopyrite) occurring interstitially between pseudomorphs of serpentine after olivine. Pentlandite commonly encloses chromite in single grains and clusters. The development of a reverse net-texture has been interpreted as a secondary (metamorphic) texture (Gillies 1993). This texture occurs where serpentine pseudomorphs are totally replaced by sulfide and serpentine occurs as a net surrounding the sulfides, in a complete reversal of the net-textured ore. None of the reversely net-textured samples in this study yielded PGM.

Disseminated ore is located above the net-textured ore and typically comprises 2–15% sulfide, occurring as lobate, fine-grained (0.1–2 mm) pentlandite and pyrrhotite situated between olivine phenocrysts. In addition, remobilized chalcopyrite forms tiny (<0.5 mm) veins and inclusions in silicate. Chalcopyrite occasionally forms interstitially between the pyrrhotite blebs. Chalcopyrite is also a common mineral at the base of internal massive sulfide horizons, where it is either concentrated in veinlets or stringers parallel to layering, or occurs within the basal sulfide interstitial to pentlandite. In addition, veins of chalcopyrite-rich massive sulfide and remobilized stringers are present below the basal massive sulfide within the Katiniq gabbro footwall. These veins occur as cusps or notches, in some cases perpendicular to the basal massive sulfide contact, and in others elongate parallel to a fault. They can be several meters in length and up to 1 m wide. Veins may comprise zones of sulfide, with chlorite, actinolite, tremolite and, in some cases, carbonate. Samples were taken from the lower chalcopyrite-rich ore below the massive sulfide and have been described as vein-ore samples, in order to distinguish between Cu-rich vein samples and secondary silicate-filled veins. The predominant vein-ore sulfide is chalcopyrite. Maucherite

(nickel arsenide) also is a common mineral in the vein chalcopyrite samples at Katiniq, and cobaltite, galena and lead and silver tellurides also occur.

The Zone 2 orebody

An assemblage of massive and disseminated sulfide similar to that at Katiniq, and displaying magmatic textures, occurs within the Zone 2 ore deposit. This was mined from an open-pit, which is now flooded. The deposit is similar in terms of geology, size and location to the open-pit workings at Zone 3 and other near-surface orebodies. The mineralization at Zone 2 occurred in five distinct pods (lenses A–E) ranging in size from 28,000 t to 1.2 Mt (Lesher 1999). All of the ore zones occur within a northeast-trending lobe of ultramafic rock, and the amount of ore was equally distributed between the basal flow unit, at or near the footwall contact, and the overlying flow units. The primary Ni–Fe–Cu mineralization consists of pyrrhotite, pentlandite and chalcopyrite, as elsewhere in the Raglan block. However, owing to the position of the orebody near the surface, we assume that erosion has removed the majority of the overlying disseminated, net-textured and reversely net-textured ore, although there is no direct evidence to support this inference. Abundant carbonate and serpentine indicate greenschist-facies metamorphism of the Zone 2 orebody, as suggested on a regional scale by Dillon-Leitch *et al.* (1986) and Barnes *et al.* (1982). The samples analyzed reflect these differences, with a proliferation of samples containing veins filled with alteration minerals cross-cutting sulfide-bearing serpentinite. In these vein samples, chalcopyrite is the most abundant sulfide. Net-textured ore in the Zone 2 orebody tends to be finer grained than that found underground at Katiniq, and it hosts 2–3 mm oikocrysts of pentlandite. As at Katiniq, the Zone 2 orebodies were sampled from deformed and undeformed zones. The former tend to be sheared fault-zones characterized in hand specimen by stretched, aligned minerals and including rod structures. Sulfide recrystallization in the direction of shear is common. Deformed samples contain large amounts of dolomite, calcite, quartz and chlorite. Pentlandite, pyrrhotite and chalcopyrite occur in roughly equal quantities in the deformed samples.

METHODS

We collected 24 hand specimens from as many rock types as possible, at each site in the Katiniq underground mine and Zone 2 open-pit. Each hand specimen was cut into blocks. Mineralogical studies were performed using conventional optical microscopy, and minerals were analyzed using a Cambridge Instruments (now Leo) S360 scanning electron microscope (SEM). Polished sections were searched systematically by eye, using the SEM set at a magnification of (100. The PGM were lo-

cated by virtue of their brightness when viewed as a back-scattered electron image. The PGM are detectable down to 0.3 μm using this method, and we assume that all PGM above 0.3 μm in each block were located. However, most of the minor phases and PGM are too small for quantitative analysis, and were identified qualitatively. Quantitative analyses of the larger PGM were made using an Oxford Instruments AN10000 EDX analyzer attached to the SEM (Table 1). Operating conditions for the quantitative analyses were: 20 kV, with a specimen-calibration current of ~1 nA and a working distance of 25 mm. A cobalt reference standard was regularly and frequently analyzed, in order to check for any drift in the analytical conditions. A comprehensive set of standards obtained from MicroAnalysis Consultants Ltd. (St Ives, Cambridgeshire) was used to calibrate the EDX analyzer. ZAF corrections were performed using an AN 10000 software program ZAF4–FLS. Images were obtained using a four-quadrant back-scattered detector operating at 20 kV, a beam current of ~500 pA, and a working distance of 13 mm, under which conditions magnifications up to 15000×are possible. The length and breadth of each PGM were measured using the electron microscope, with the area of each PGM calculated using the equivalent circle diameter (ECD). To place the PGM in context mineralogically, the associated silicate and sulfide minerals were identified qualitatively using the SEM.

TABLE 1. RESULTS OF SEMIQUANTITATIVE ANALYSES OF PLATINUM-GROUP MINERALS AND MAUCHERITE, KATINIQ AND ZONE 2 ORES, CAPE SMITH, QUEBEC

	1	2	3	4	5	6	7	8
Pt wt%	51.5	55.0	55.5					
Pd				43.8	43.9	26.5	26.4	0.8
Rh	2.1	1.0						
Ni			0.9					50.7
Cu						1.5		
Co								0.5
Fe	2.5	0.9	1.3			1.4		0.3
S		0.7						
As	39.8	42.2	41.4					46.9
Bi				6.3	3.8	9.7	9.0	
Te				8.2	2.3	62.1	64.8	
Sb	3.7	0.3		42.7	48.8			
Hg								
Total	99.6	100.1	99.1	101.0	98.8	101.2	100.2	99.2

1) RA7C Sperrylite $(Pt_{0.94}Rh_{0.07})_{\Sigma1.01}(As_{1.88}Sb_{0.11})_{\Sigma1.99}$, host mineral: pyrrhotite (Fe not included in calculation).
2) RA21B Sperrylite $(Pt_{0.99}Rh_{0.04})_{\Sigma1.03}As_{1.98}$, host mineral: pentlandite (Fe, S not included in calculation).
3) RA28A Sperrylite $Pt_{1.01}As_{1.98}$, host mineral: pentlandite (Fe, Ni not included in calculation).
4) RA29A Sudburyite $Pd_{0.96}(Sb_{0.83}Te_{0.15}Bi_{0.07})_{\Sigma1.04}$, host mineral: maucherite.
5) RA29C Sudburyite $Pd_{0.97}(Sb_{0.94}Te_{0.04}Bi_{0.04})_{\Sigma1.02}$, host mineral: maucherite.
6) RA20 Merenskyite $Pd_{0.95}(Te_{1.87}Bi_{0.18})_{\Sigma2.05}$, host mineral: chalcopyrite (Fe, Cu not included in calculation).
7) RA20C Merenskyite $Pd_{0.93}(Te_{1.91}Bi_{0.16})_{\Sigma2.07}$, host mineral: chalcopyrite
8) RA29A1 Pd-bearing maucherite $(Ni_{10.86}Pd_{0.09}Fe_{0.06}Co_{0.10})_{\Sigma11.11}As_{7.88}$

The Platinum-Group Minerals

During this investigation, nine different PGM (and a gold–silver alloy) were identified, using the SEM data on 42 grains. The PGM present in the samples are predominantly sperrylite ($PtAs_2$), sudburyite (PdSb) and merenskyite ($PdTe_2$). Only one of these grains is composite, composed of sperrylite and sudburyite. Small grains of rare PGM (only occurring once or twice in the samples) were analyzed only semiquantitatively, because results include substantial contributions of elements from surrounding minerals. These rarer minerals were tentatively identified as moncheite ($PtTe_2$), temagamite (Pd_3HgTe_3), Pd bismuth tellurides, possibly maslovite and michenerite, and an unnamed Pd–Pb bismuth telluride. Maucherite ($Ni_{11}As_8$) was found to contain up to 1% Pd. A Pt–Os–Ru-bearing sulfarsenide, probably hollingworthite, also is present. These PGM are described in the following paragraphs, and the compositions of some of the larger PGM are given in Table 1.

Sperrylite

Sperrylite crystals vary considerably in shape and size and are enclosed in a variety of host minerals (Fig. 2a). They are usually closely associated with base-metal sulfide and are commonly at the edge and partially enclosed by pentlandite, pyrrhotite or chalcopyrite. Within chalcopyrite in the vein-ore samples, sperrylite forms larger crystals of up to 40 μm (Fig. 3a). Adjacent to sulfide grains, sperrylite is subhedral to euhedral, showing angular blocky shapes with smoothly curved edges and slightly rounded corners. However, where the sperrylite is in contact with altered silicate adjacent to the host sulfide, the morphology of the crystals becomes irregular, and the blocky crystals are truncated. Thus, part of the sperrylite crystals has been removed, probably by dissolution, where they are in contact with altered silicate (Fig. 2a; i–v). Laths of actinolite or tremolite aligned adjacent to the sperrylite also seem to truncate the sperrylite, giving it straight edges adjacent to the lath. The greater the proportion of a sperrylite crystal surrounded by secondary silicate, the more irregular the outline of the sperrylite becomes. In deformed samples, clusters of irregularly shaped sperrylite lie across parallel elongate rows of secondary silicates including actinolite, tremolite, chlorite, and serpentine and sulfide (Figs. 3b, 2a; ix, x). A very irregular grain of sperrylite adjacent to an irregular grain of sudburyite is enclosed by biotite and surrounded by zoned calcite that has a botryoidal surface, with convex surfaces protruding into the biotite (Fig. 3c). The composition of sperrylite agrees with those given by Cabri (2002). Up to 2.1 wt% rhodium is found to substitute for platinum in all but one of the sperrylite grains analyzed from both the Katiniq and Zone 2 orebodies. Varying amounts of Sb also are present (Table 1, anal. 1–3).
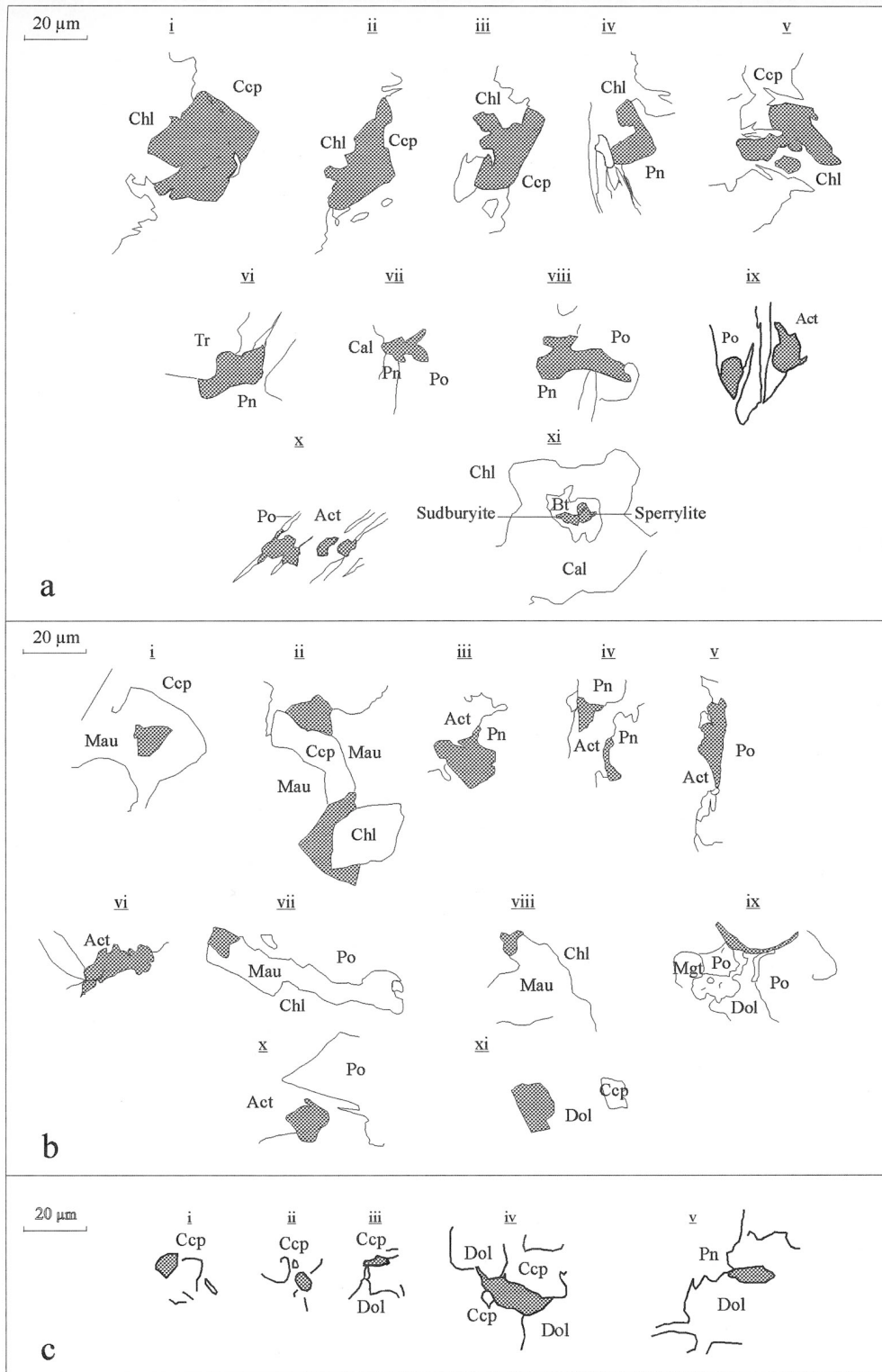
Sudburyite

Sudburyite crystals occur in vein, net-textured and deformed ore (Fig. 2b). They are located adjacent to grains of base-metal sulfide and, where partially enclosed, have a blocky form with an almost euhedral shape, similar to that described for the sperrylite enclosed in sulfide. Where sudburyite is adjacent to altered silicate, its edges are irregular. Sudburyite in Zone 2 is either at the edge or surrounded by dolomite (Fig. 3d), whereas at Katiniq, the sudburyite is surrounded by calcite and strongly associated with maucherite. Sudburyite was identified in each of the occurrences of maucherite, where it mostly lies in contact with the maucherite and in one case is enclosed by it (Fig. 3e). Maucherite contains up to 1% Pd. Sudburyite invariably contains up to 6.3 wt% Bi and up to 8.2% Te (Table 1), within the ranges given by Cabri (2002).

Merenskyite

Merenskyite is present as subhedral to anhedral crystals that are almost exclusively associated with chalcopyrite, rather than pyrrhotite or pentlandite (Fig. 2c). A Pd telluride, too small to obtain a quantitative analysis, is located within a Ag telluride associated with chalcopyrite. In another case, the merenskyite has a crystal of Ag telluride adjacent to it, and both are surrounded by chalcopyrite. Merenskyite also occurs in association with dolomite, either completely enclosed within it (Fig. 3f) or at the junction between chalcopyrite and dolomite. The merenskyite (Table 1) contains varying proportions of Bi, up to 10 wt%.

Rare PGM

Only one grain of moncheite was found, in disseminated ore in the Katiniq orebody, as a subhedral grain 9 μm across in silicate. A round grain 1 μm across of Pd–Hg telluride, possibly temagamite, was located in a deformed and sheared sample. It is associated with silicate but enclosed by pyrrhotite. An elongate grain of a Pd–Bi telluride, possibly maslovite, is aligned parallel to the edge of a pentlandite crystal, in a sample of massive sulfide. Another Pd–Bi telluride, possibly michenerite, occurs as subhedral inclusions in pyrrhotite, in a sample of vein ore from Katiniq. In the same sample, an unnamed Pd–Pb telluride occurs in chalcopyrite and shows evidence of dissolution where a part of the grain is in contact with a silicate phase. Grains of an Rh–Pt–Os–Ru-bearing sulfarsenide, possibly hollingworthite, <2 μm across, are located along the cleavage of pyrrhotite adjacent to altered silicate.
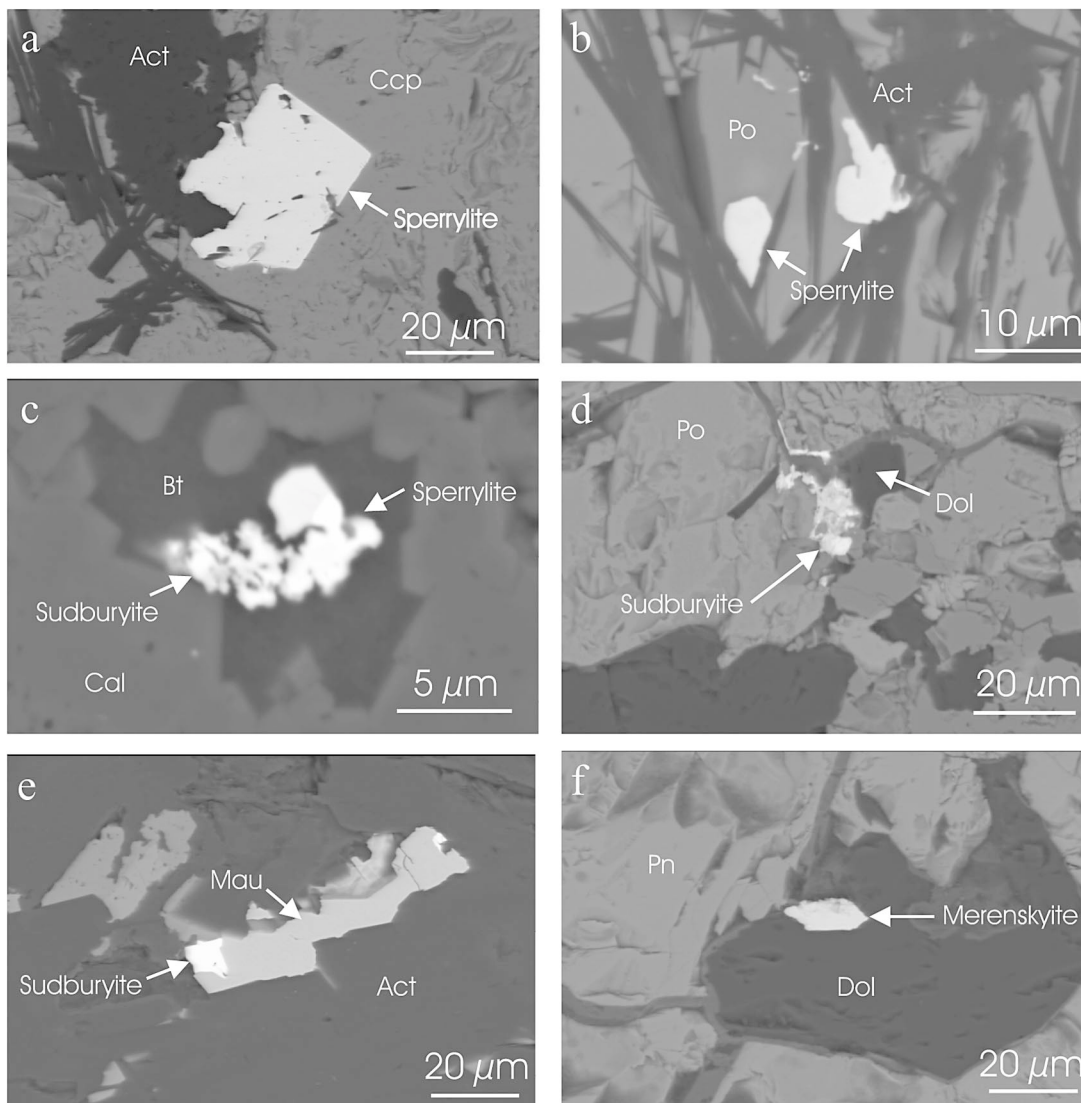
a

20 µm

i — Chl, Ccp

ii — Chl, Ccp

iii — Chl, Ccp

iv — Chl, Pn

v — Ccp, Chl

vi — Tr, Pn

vii — Cal, Pn, Po

viii — Po, Pn

ix — Po, Act

x — Po, Act

xi — Chl, Sudburyite, Bt, Sperrylite, Cal

b

20 µm

i — Ccp, Mau

ii — Ccp, Mau, Mau, Chl

iii — Act, Pn

iv — Pn, Act, Pn

v — Po, Act

vi — Act

vii — Mau, Po, Chl

viii — Chl, Mau

ix — Mgt, Po, Po, Dol

x — Po, Act

xi — Dol, Ccp

c

20 µm

i — Ccp

ii — Ccp

iii — Ccp, Dol

iv — Dol, Ccp, Ccp, Dol

v — Pn, Dol

FIG. 3. Back-scattered electron microscope images. a) Sperrylite, euhedral where it is enclosed in chalcopyrite. Note the irregular edge of the sperrylite where it is in contact with actinolite–tremolite. b) Altered silicate (actinolite–tremolite) traversing sperrylite and pyrrhotite. c) Irregular composite grain of sperrylite and sudburyite enclosed in biotite and calcite. d) Irregular sudburyite at the boundary between pyrrhotite and dolomite. e) Typical association of sudburyite with maucherite (NiAs). f) Merenskyite enclosed within dolomite. Symbols as in Figure 2.

The relative abundances of PGM

FIG. 2. Sketches of PGM grains (shaded) showing the range of textures and host minerals. a) Sperrylite grains, b) Sudburyite grains, c) Merenskyite grains. Symbols: Act: mineral belonging to the actinolite–tremolite group, Bt: biotite, Cal: calcite, Ccp: chalcopyrite, Chl: chlorite, Dol: dolomite, Mau: maucherite, Mgt: magnetite, Pn: pentlandite, Po: pyrrhotite.

Sperrylite is the most abundant mineral, according to surface area, followed by sudburyite and merenskyite (Fig. 4a). Sperrylite comprises 34% of all the PGM grains identified. The rare PGM are grouped together and constitute approximately 17%, although individually only one or two grains of each were found. Figures 4b and 4c show the relative abundances of the PGM in
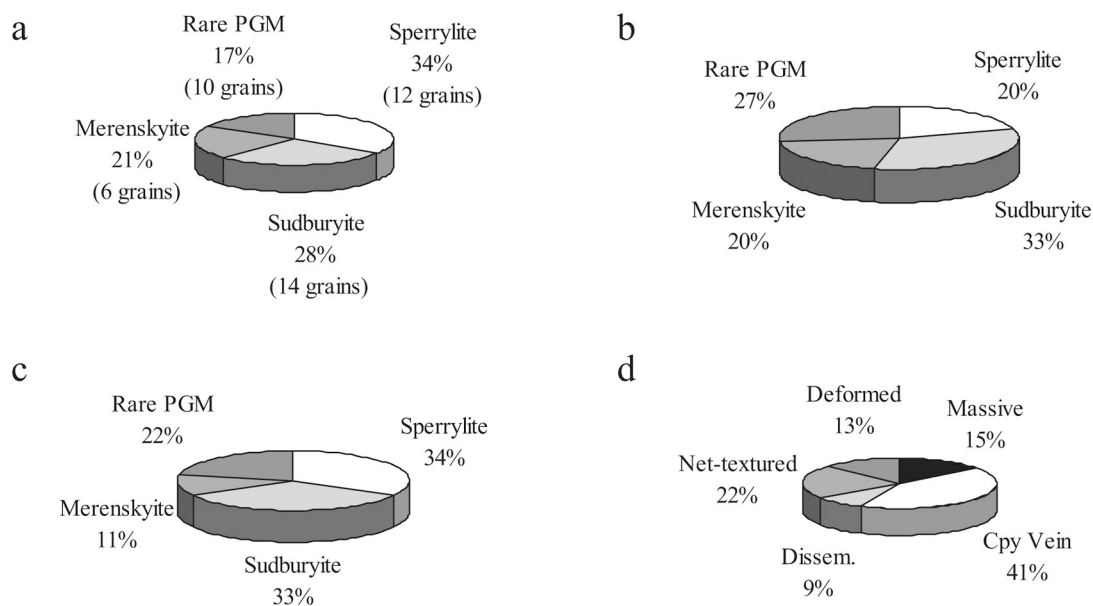
a

Rare PGM
17%
(10 grains)

Sperrylite
34%
(12 grains)

Merenskyite
21%
(6 grains)

Sudburyite
28%
(14 grains)

b

Rare PGM
27%

Sperrylite
20%

Merenskyite
20%

Sudburyite
33%

c

Rare PGM
22%

Sperrylite
34%

Merenskyite
11%

Sudburyite
33%

d

Deformed
13%

Massive
15%

Net-textured
22%

Dissem.
9%

Cpy Vein
41%

FIG. 4.   Relative abundances of PGM a) according to surface area (Katiniq and Zone 2), b) according to grain count, in the Zone 2, and c) in the Katiniq orebody, and d) according to ore type.

a

b
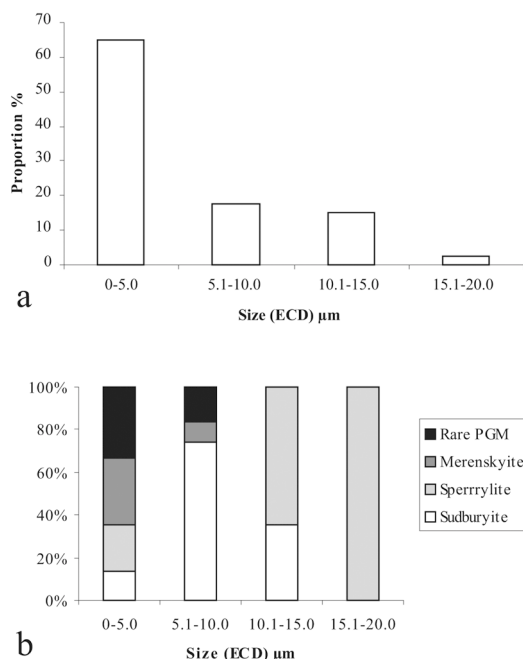
FIG. 5.   a) Size distribution of total PGM, and b) distribution of PGM in size ranges of the Katiniq and Zone 2 orebodies combined.

the two orebodies based on grain counts. Notably, sperrylite is more abundant in the Katiniq orebody, and merenskyite is more abundant in the Zone 2 orebody.

The relative number of grains of each PGM by ore type is shown in Figure 4d. A significant quantity of the minerals, 41%, occurs in the vein ores (70% by area). These ores also show the widest range of minerals, with michenerite and a Pd–Pb telluride occurring as well as sperrylite and sudburyite. Net-textured ore contains the next highest proportion of PGM, followed by massive samples. Sheared and deformed ores contain 10% of the PGM. Merenskyite occurs exclusively in secondary, deformed, silicate-filled veins, along with minor sudburyite and the single grain of temagamite. Two-thirds of the PGM grains in the massive ore consist of sperrylite. Disseminated ore contains only one grain of moncheite. Michenerite occurs solely in Cu-rich vein ore.

The size distribution of PGM

All grain sizes were measured using the equivalent circle diameter (ECD). Using this method, the average grain-size of the PGM is 10.8 μm, the largest measuring 37.4 μm. Over half the PGM lie within the 1–5 μm (ECD) range, 17.5% are between 5 and 10 μm, and only 2.5% are over 15 μm (ECD) in size (Fig. 5a). However, no individual group of minerals conforms exactly to these ranges (Fig. 5b). Merenskyite along with the rare

PGM identified account for over half of the smaller grains (below 5 mm), whereas the largest minerals are dominantly sperrylite and, to a lesser extent, sudburyite. Sperrylite has an average grain-size of 15.8 μm (ECD), sudburyite, 12.6 μm (ECD), and merenskyite, 7.0 μm (ECD).

The size distribution of the PGM grains varies between the two orebodies. The sperrylite grains are much larger in the Katiniq deposit than in Zone 2, with average grain-sizes of 17.8 and 7.2 μm (ECD) respectively. The grain size of sudburyite is more evenly distributed, with an average of 14.0 μm at the Katiniq site and 10.8 μm in Zone 2. The merenskyite and rare PGM together are also evenly distributed in terms of grain size, with an average of 6.4 μm in the Katiniq deposit and 6.8 μm in Zone 2.

Host minerals of the PGM

Many minerals host the PGM; 30% of the PGM (by area %) are totally enclosed within a base-metal sulfide. The majority of these grains, >60%, are associated with chalcopyrite, although chalcopyrite is not the most abundant base-metal sulfide. Only 17.5% of PGM are enclosed wholly within chalcopyrite or pentlandite, and are thus the only PGM certain to be recovered. Also, 41% (by area) are located at a boundary between a silicate phase and a sulfide phase. Over 50% of these are located between pentlandite and silicate. Only 7% are totally enclosed within silicates, with 9% associated with maucherite and 13% associated with carbonates. Thus the PGM in the silicates and carbonates (20%) may not be recoverable, and the PGM associated with maucherite also may be lost, depending on the behavior of maucherite during flotation.

The minerals that host the PGM differ between the Katiniq orebody and Zone 2 (Figs. 6a, b). The majority of the carbonates occur in the Zone 2 ore. The PGM generally occur at the boundary between dolomite and a base-metal sulfide; in this orebody, the majority of these PGM grains consist of merenskyite and some sudburyite. Carbonate minerals do occur in the Katiniq samples, but no PGM were observed in contact with them. Maucherite was only identified in samples from the Katiniq orebody, and is strongly associated with chalcopyrite. All of the PGM grains occurring within or adjacent to maucherite consist of sudburyite. At Katiniq, more PGM grains occur at silicate–sulfide boundaries, and fewer occur enclosed in sulfides, than in the Zone 2 area. Sudburyite and merenskyite occur preferentially in altered carbonate-bearing rocks, and sperrylite is more common in vein, net-textured and massive ores. The correlation between chalcopyrite and PGM is in accordance with the observation that both chalcopyrite and PGM occur toward the edges of compound sulfide clusters. Several of the rare PGM occur as tiny blebs within pyrrhotite, not along discernible grain-boundaries.

DISCUSSION

The most common PGM at Raglan, sperrylite (PtAs$_2$), sudburyite (PdSb) and merenskyite (PdTe$_2$), are also minerals that are commonly described from other major PGE deposits, including the Bushveld, and from PGE-bearing magmatic sulfide deposits such as Sudbury and Noril'sk (Cabri 2002).

Magmatic fractionation of PGE

Sulfide liquids are known to separate from silicate magmas, and crystallize to produce a monosulfide solid-solution (MSS) and a fractionated Cu-rich sulfide liquid (Mostert *et al.* 1982). The subsequent crystallization of the latter leads to an intermediate solid-solution (ISS) (Skinner *et al.* 1976). Cooling of the MSS results in the exsolution of pentlandite from pyrrhotite, with the PGE held in solid solution forming PGM during the exsolution process, as demonstrated experimentally by Makovicky (2002). The ISS exsolves chalcopyrite and cubanite as it cools, and the PGE are exsolved to form PGM. The crystallization of an immiscible sulfide liquid causes the PGE to fractionate (Fleet *et al.* 1993, Barnes *et al.* 1997b). The MSS tends to be richer than
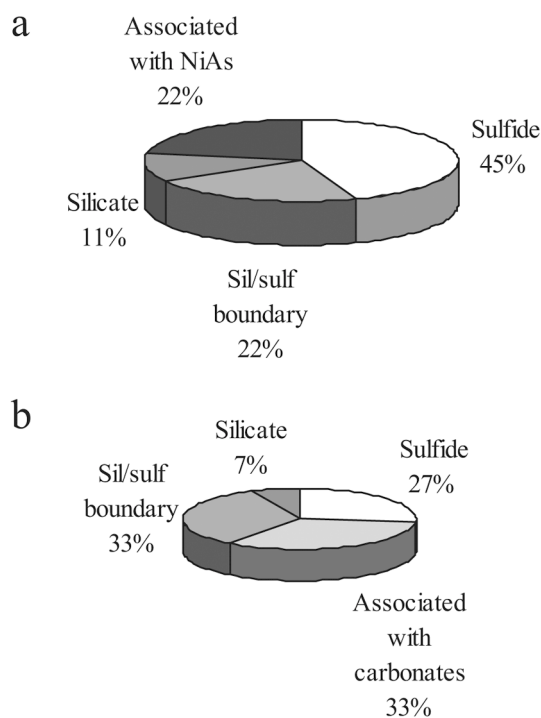

FIG. 6.   Mode of occurrence of PGM a) in the Katiniq, and b) in the Zone 2 orebodies.

ISS in Os, Ir, Ru and Rh-bearing PGM, owing to low partition-coefficients in the latter (Barnes *et al.* 2001). Pd, Pt, Au, and Cu are incompatible elements and are thus preferentially partitioned in the sulfide liquid during the crystallization of a MSS. Therefore, PGM associated with Cu-rich sulfide tend to be Pt- and Pd-rich (Li & Naldrett 1993a, Li *et al.* 1996, Barnes *et al.* 1997a). Thus the PGM in magmatic sulfide deposits should reflect this behavior, provided alteration has not remobilized the PGE.

At Raglan, sulfide ores consistently show the presence of stringers of chalcopyrite at the base of the massive sulfides and at the boundary between massive and net-textured ore. Along with the presence of minimal amounts of chalcopyrite in the massive ore, this distribution is consistent with the components of chalcopyrite accumulating in a fractionated sulfide liquid once MSS crystallized out first. At Katiniq and Zone 2, both Pt- and Pd-bearing minerals are present in the pentlandite–pyrrhotite assemblage. These elements thus were held in the MSS and did not fractionate completely into the Cu-rich liquid. Blebs of PGM within the Fe- and Ni-rich sulfides were probably exsolved *in situ* from the pyrrhotite and pentlandite. In this study, we indicate that Pt is the main PGE present in chalcopyrite in Cu-rich vein ores, implying a level of partitioning of Pt into the ISS liquid. Palladium occurs more commonly in late ore-veins. The minor concentrations of Rh, Os and Ru in hollingworthite associated with pyrrhotite indicate that these elements fractionate into the MSS, in agreement with the findings of Cabri & Laflamme (1976) and Barnes *et al.* (1997a).

As, Te, Bi and Sb and the effects of low-temperature alteration

Elements such as As, Te, Sb, Bi partition into an immiscible sulfide melt when it separates from the siliceous magma, as for example in the Sudbury ores (Cabri & Laflamme 1976, Li & Naldrett 1993a, Jago *et al.* 1994). During crystallization of an immiscible sulfide liquid, Cu fractionates from Ni, but also As, Te, Bi and Sb fractionate and predominantly concentrate in the Cu-rich liquid. Minerals bearing As, Te, Bi and Sb form, especially PGM, at the edges of sulfides, principally chalcopyrite (Li & Naldrett 1993a). A large proportion of the PGM identified in this study occurs at silicate–sulfide grain-boundaries, at sulfide grain-boundaries, or near the edge of sulfide minerals, and are As-, Te-, Bi- and Sb-bearing. However**,** As-, Te-, Bi- and Sb-bearing PGM are associated with pentlandite, pyrrhotite as well as chalcopyrite.

The PGE retained in solid solution within MSS and ISS eventually exsolve at lower temperatures. Therefore, on cooling, they appear as PGM within or in close proximity to the sulfides (Makovicky *et al.* 1985, Czamanske *et al.* 1992, Prichard *et al.* 1994). Hence, it is likely that in the Katiniq and Zone 2 samples, the PGE

formed discrete minerals by exsolution from solid solution rather than crystallizing as primary magmatic phases. Formation of discrete minerals also may have occurred as a result of low-temperature metamorphic recrystallization.

An extensive replacement of primary silicate assemblages is observed, with chlorite and serpentine commonly developed, possibly as a result of regional metamorphism (Dillon-Leitch *et al.* 1986). Evidence for low-temperature hydrothermal alteration is seen in the recrystallization of sulfides around silicate intergrowths and the presence of minerals such as chlorite, cross-cutting sulfides. In addition, the presence of large amounts of serpentinite throughout the Raglan area is indicative of extensive hydrothermal activity.

There is ample textural evidence in the Raglan samples to indicate that the PGM have been affected by metamorphic recrystallization. The truncation of blocky sperrylite and sudburyite where they are in contact with altered silicate, along with the irregular outlines of crystals of the PGM surrounded by secondary silicates, suggest modification of the PGM.

Remobilized PGE

Secondary-silicate-filled veins commonly occur at the contact between ore types owing to changes in competency that existed at the time of formation (Dillon-Leitch *et al.* 1986). Deformed or sheared samples contain talc and abundant carbonates, particularly dolomite, particularly from the Zone 2 pit. The PGM that occur within carbonates may have been modified *in situ* during carbonate formation, or they may be relict minerals that have not been modified by replacement of the silicates surrounding them. It is unclear which process has occurred. However, they may also have been precipitated with these low-temperature carbonates. The majority of PGM that occur infrequently throughout the rest of the Katiniq and Zone 2 orebodies, along with sudburyite, are most common in the late carbonate-filled veins and sheared ores.

The mobilization of PGE by processes involving an aqueous fluid has been well documented (Wood 2002 and references therein), and numerous studies indicate that Pd exhibits preferential mobility in a number of hydrothermal environments (*e.g.*, Li & Naldrett 1993b, McDonald *et al.* 1999, Byrne & Yao 2000). Experimental and empirical data have shown that Pd is preferentially mobilized over Pt (*e.g.*, Cousins 1973, Fuchs & Rose 1974, Cousins & Vermaak 1976), with Pd complexes destabilizing more readily than Pt complexes (Sassani & Shock 1998). However, it has been shown that Pt is highly soluble in Cl-rich aqueous fluids at temperatures between 25° and 300°C (Wood 1987, Mountain & Wood 1988, Wood *et al.* 1989, 1994, Gammons *et al.* 1992). The PGM assemblage in secondary veins in the Katiniq and Zone 2 orebodies strongly supports the evidence that Pd is more mobile than Pt.

Pd-bearing maucherite forms only in secondary, deformed veins in postmagmatic shear-zones as part of a low-temperature assemblage of minerals. The Pd present in maucherite must have been remobilized at a low temperature. Discrete grains of sudburyite are strongly associated with maucherite (Fig. 3e). The presence of Pd in maucherite indicates that the Pd was incorporated into the maucherite as it formed during shearing. The presence of Pd-bearing sudburyite in association with maucherite suggests that Pd was subsequently partially ejected from the maucherite to form Pd-bearing PGM. Conversely, sudburyite may have formed at the same time as the maucherite, but an excess of Pd saturated the maucherite, resulting in PGM forming at its edges.

The complete absence of any other detectable PGE with maucherite may suggest that Pd is more mobile at low temperatures. However, this is speculative, as the analytical technique does not detect trace amounts of PGE. It must be noted that nickel arsenide is not present in any significant quantities in the Raglan deposit as a whole.

CONCLUSIONS

1. Sperrylite, sudburyite and merenskyite are the most common PGM in the Katiniq and Zone 2 orebodies of the Raglan block (34, 28 and 21% by area, respectively). Although there is local variation between the two orebodies, the PGM described here are similar to those in other areas in the Raglan block.

2. The primary concentration of the PGE is derived entirely from the magma.

3. Textural features of the PGM and base-metal sulfides indicate that a large number of PGM have been modified by low-temperature alteration.

4. The presence of PGM in carbonate veins and shear zones suggests the remobilization of Pd.

5. Heavily faulted areas, as illustrated by samples from Zone 2, are likely to contain more Pd antimonides and tellurides locked in carbonate or silicate gangue, resulting in perhaps 20% (by area) of the PGM being unrecoverable owing to complete enclosure in gangue minerals.

6. Only 17.5% (by area) of the PGM in this study are certain to be recovered during froth flotation, owing to enclosure in chalcopyrite or pentlandite.

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