

## DISTRIBUTION OF PGE IN PYROXENE-BEARING ULTRAMAFIC CUMULATES IN THE THETFORD MINES OPHIOLITIC COMPLEX, QUEBEC

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### ABSTRACT

New geochemical results on the distribution of platinum-group elements (*PGE*) in ultramafic cumulates of the Thetford Mines ophiolitic complex (TMOc), in southeastern Quebec, are presented in order to assess magmatic *versus* hydrothermal contributions of *PGE* in pyroxene-bearing ultramafic cumulates. Pt (70–130 ppb) and Pd (75–130 ppb) are irregularly distributed and are not correlated with low S content (0–700 ppm) or rock type. However, C1-chondrite-normalized patterns suggest that Pd and Ir contents correlate with clinopyroxene and olivine fractionation, respectively. We suggest that primary magmatic *PGE* are affected by intense hydrothermal circulation that occurred throughout the cumulates. *PGE* contents in pyroxene-bearing ultramafic cumulates are, on average, higher than values reported for similar rocks of other ophiolitic complexes. This observation is consistent with derivation of Mg-rich melts from partial melting of a refractory mantle source characteristic of an arc environment. Owing to their greater resistance to erosion than olivine-rich rocks, pyroxene-bearing cumulates provide good geochemical indicators for potentially economic *PGE* concentrations in underlying poorly exposed dunitic parts of the pile of cumulates.

**Keywords:** platinum-group elements, Thetford Mines, ophiolite, ultramafic cumulates, arc, hydrothermal alteration, Quebec.

### SOMMAIRE

Des données nouvelles sur les teneurs en éléments du groupe du platine (*EGP*) dans les cumulats ultramafiques du complexe ophiolitique de Thetford Mines (COTM), dans le sud-est du Québec, sont présentées pour discerner l'importance relative des processus magmatiques et hydrothermaux sur les concentrations des *EGP*. Le Pt (70–130 ppb) et le Pd (75–130 ppb) sont distribués irrégulièrement et ne montrent pas nécessairement une corrélation avec les faibles teneurs en soufre (0–700 ppm) ou le type de roche. Cependant, le profil normalisé à la chondrite C1 fait penser que les teneurs élevées en Pt et Ir coïncident avec le fractionnement du clinopyroxène et de l'olivine, respectivement. Nous proposons que les *EGP* primaires sont mobilisés par

une circulation hydrothermale intense ayant affecté les cumulats. Les teneurs en *EGP* des cumulats de la série pyroxénitique sont, en moyenne, plus élevées que celles publiées pour des roches similaires d'autres complexes ophiolitiques. Cette observation est en accord avec l'origine des magmas magnésiens par la fusion partielle d'un manteau réfractaire caractéristique d'un environnement d'arc. Les cumulats pyroxénitiques, plus résistants à l'érosion que les cumulats riches en olivine, seraient de bons indicateurs géochimiques de concentrations potentiellement économiques en *EGP* dans les cumulats dunitiques lités sous-jacents, qui n'affleurent généralement pas bien.

**Mots-clés:** éléments du groupe du platine, Thetford Mines, ophiolite, cumulats ultramafiques, arc, altération hydrothermale, Québec.

### INTRODUCTION

The Lower Ordovician Thetford Mines ophiolitic complex (TMOc) is an ultramafic-mafic massif situated within the Baie Verte – Brompton line of the Quebec Appalachian belt (Williams & St-Julien 1982), about 100 km south-southwest of Quebec City. The total thickness of the complex is about 8 km. The complex consists of 800 meters of magmatic cumulates, which are in faulted contact with 5 km of upper mantle, dunitic and harzburgitic peridotitic tectonites (Laurent 1975a). The cumulate zone is characterized by a polycyclic alternation of layers of chromitite, dunite, wehrlite, pyroxenite, gabbros and orthopyroxene-rich dikes and sills. A dike-sill complex (100 m) composed of diabase, diorite, plagiogranite, and amphibolitic gabbros overlies the stratiform zone of cumulates. The upper unit of the TMOc is characterized by two groups of volcanic rocks, each covered by sedimentary units (Fig. 1; Laurent & Hébert 1989). The TMOc was thrust over the North American continental margin in Ordovician times and was partly dismembered into the Saint-Daniel *mélange*, correlated with middle Ordovician calc-alkaline volcanic arc sequences to the southeast (Tremblay *et al.* 1989). The TMOc is considered to have formed in a complex intraoceanic arc environment (Laurent & Hébert 1989, Hébert & Laurent 1989).

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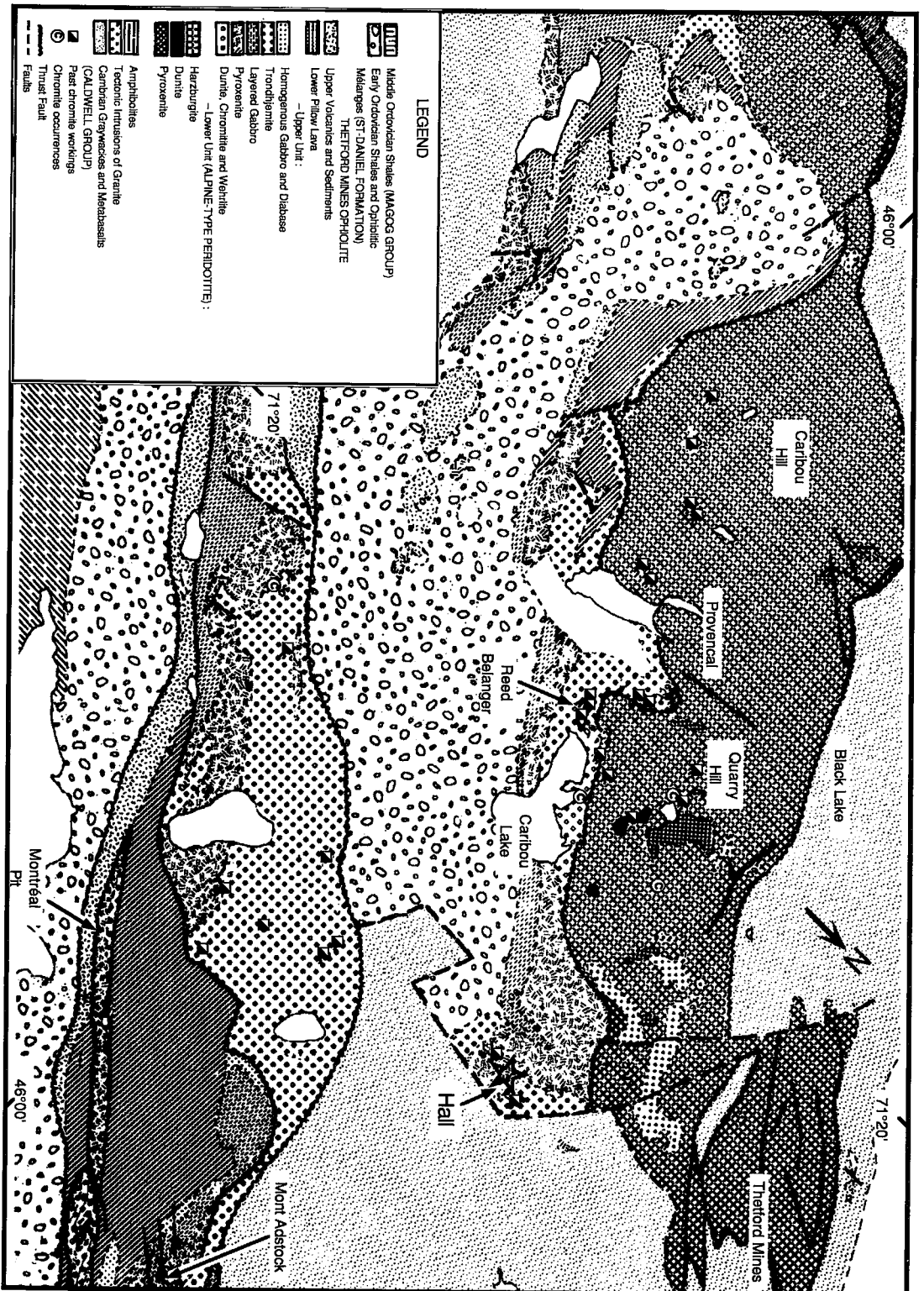


FIG. 1. Simplified geological map of TMOG after Laurent & Kaçira (1987). Star indicates the location of stratigraphic columns presented in Figure 2.

The aim of this study is to provide new geochemical data on the platinum-group elements in rocks from the layered cumulate zone. An exceptionally well-layered sequence of dunitic, wehrlitic and pyroxenitic rocks is exposed north and stratigraphically above the Hall chromite orebody (Fig. 1). This zone is located 5 km to the south of Thetford Mines, in Coleraine Township, on the south flank of the Red Hills. A platinum anomaly was discovered by Resources Coleraine in the Hall chromite orebody, associated with the dunitic basal cumulate (Gauthier *et al.* 1990). The analysis of a chromitite sample revealed a maximum content of 2 g/t Pt. The area is still under investigation. This study of a restricted area covering a specific horizon (290 m) (Fig. 2) was initiated in order to test the consanguinity of rocks in this layered sequence and to understand the anomalous concentration of platinum-group elements (PGE) at a level where pyroxene is a major fractionating phase.

#### SAMPLE DISTRIBUTION

Sixty representative samples were collected from the section of cumulates outcrops. The first twenty-four of these are widely spaced and collected from throughout the sequence of cumulates in order to establish the distribution of PGE from the base to the top of the sequence. The second suite of samples is composed of thirty-six closely spaced specimens taken from the layered sequence near the top of area (Fig. 2). The purpose of this sampling program is to verify if two or more liquids are involved in the fractionation of the magmatic sequence. If a single magma is involved, geochemical variations will be similar and not complex in terms of stratigraphy.

#### FIELD AND MICROSCOPIC OBSERVATIONS

The dunite, wehrlite and clinopyroxenite cumulates are cut by orthopyroxene-rich dikes that turn into sills stratigraphically higher in the sequence of cumulates. The alteration surface of the dunite is greyish to dark brown, and the fresh surface is dark green to black. For wehrlite and pyroxenite, the alteration surfaces are brown to reddish brown, and fresh surfaces are yellow-green. The thickness of individual layers is variable. In the upper part of the pyroxenitic sequence, the layers are cm- to dm-thick, but other outcrops show m-thick bedding (Fig. 3a). In the latter case, the wehrlite and clinopyroxenite are the most common rock-types. Bedding continuity along strike and the significance of faults are unknown at present. In samples collected from these outcrops, secondary minerals are dominant. Only sparse clinopyroxene, chromite and orthopyroxene grains

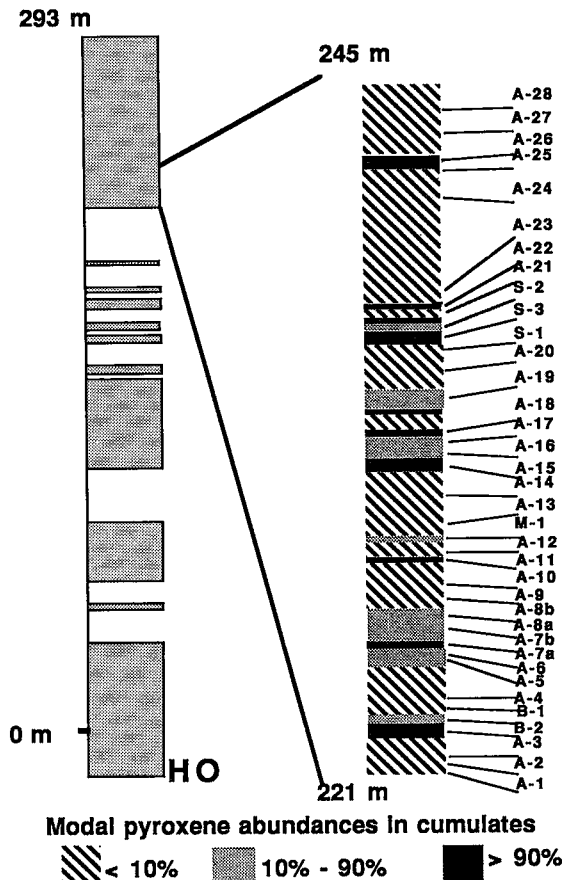


FIG. 2. Stratigraphic columns of ultramafic-mafic cumulates and position of samples. HO: Hall chromite orebody. Blank spaces represent covered segments of the section studied.

are preserved. We find serpentine (Fig. 3b) and tremolite (not illustrated) as the main secondary phases. Chromite grains are fractured and recrystallized to magnetite and "ferrichromite" along cracks and the outer rim of grains. Very fine polymetallic phases are observed in this secondary magnetite (see also Corrivaux & Laflamme 1990). Three phases of serpentinization are recognized (Fig. 3d). The first phase is pervasive and affects the whole rock without significant increase in volume. Mesh textures after olivine and pseudomorphic replacement of pyroxene are typical. The second and third phases are controlled by opening of fissures, which are filled with fibrous chrysotile. A magnetite seam appears in the center of the veins. These textures indicate a system of extensional stresses (Laurent 1975b). Iron, no longer accommodated in silicate phases during hydration, is released to form minute grains of magnetite.

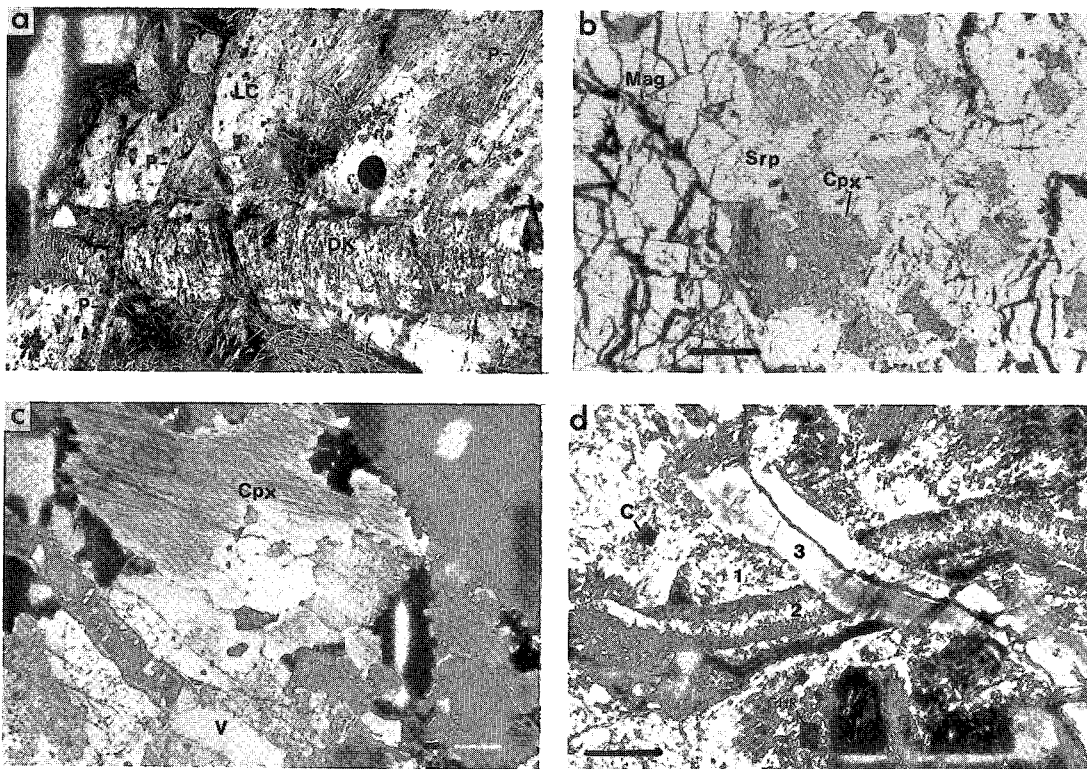


FIG. 3. a) Photograph of layered cumulates (LC) and cross-cutting orthopyroxene-rich dike (DK). Lens cap is 50 mm across. P: pyroxenitic layer. b) Photomicrograph of dunitic (left) and wehrlitic (right) cumulates. Note the polygonal serpentinization texture in dunite and preserved poikilitic texture in wehrlite. Scale is 1 mm long. Mag magnetite, Srp serpentine, Cpx clinopyroxene. c) Photomicrograph of clinopyroxenite. Note the preserved partly recrystallized adcumulus texture and late serpentine veinlet (V). Scale bar is 1 mm long. d) Photomicrograph of three stages of serpentinization: 1) pervasive lizardite replacement of olivine, 2) poorly crystallized serpentine, 3) fibrous chrysotile. Scale bar is 1 mm long. C chromite.

The upper part of the ultramafic sequence is better preserved (Fig. 2). Pyroxenitic rocks are fresh. The diopside crystals are recrystallized into neoblasts only at their margins and are compositionally heterogeneous (Fig. 3c). The enstatite is serpentinized. Lizardite and minor antigorite are the main varieties of serpentine observed as pseudomorphs (Fig. 3b). This part of the sequence of cumulates presents a well-preserved primary adcumulus texture.

The upper part of the sequence of ultramafic cumulates is characterized by varieties of late-stage pyroxenitic intrusive bodies. Dikes, 1 to 30 cm across, are fine grained at contacts with layered rocks and coarser grained (1–10 cm) in the center. In thin section, large crystals of fresh enstatite are observed. Partly altered olivine and clinopyroxene surround orthopyroxene grains. The dikes are undeformed, and no deformation texture is observed. The emplacement of dikes within the main sequence of cumulates seems to have occurred before a complete

cooling of main sequence because of the absence of chilled margins and the presence of associated sills derived from discordant intrusive feeder dikes. The study of the dike–sill network is still under investigation.

#### ANALYTICAL TECHNIQUES

Concentrations of major and minor elements were determined by X-ray fluorescence at the Centre de Recherche Minérale du Québec (C.R.M.Q.). Concentrations of the trace elements (Co, Cr, Ni and Sc) and PGE (Os, Ir, Ru, Rh, Pt, Pd and Au) were determined by neutron activation at the Institut National de la Recherche Scientifique (INRS), secteur Géoresources. We used a Ni-sulfide preconcentration with 50 grams of sample for PGE analyses (Hoffman *et al.* 1978). We used more powder (10 times the weight used by Oshin & Crocket 1982) in our analyses. We

TABLE 1. TRACE ELEMENT CONTENTS OF ULTRAMAFIC CUMULATES<sup>1</sup>

	RT**	ppb*							ppm					Co (Co+Sc)	Mg#	Ni	Pd
		Ir	Ru	Rh	Pt	Pd	Au	PGE+Au	Co	Cr	Ni	Sc	S				
A-28 D		3.1	-	9	42	54	11	119.1	125	5008	1490	11	700	0.92	0.80	11.9	17
A-27 D		4.4	21	10	71	78	8	192.4	139	5071	1333	9	700	0.94	0.80	9.6	18
A-26 P		-	-	-	8	19	10	37.0	72	4074	505	64	0	0.53	0.75	7.0	-
A-25 D		3.8	36	10	71	90	15	225.8	134	3886	1582	12	700	0.92	0.81	11.8	24
A-24 D		1.8	36	5	31	-	10	83.8	146	3500	1417	11	200	0.93	0.76	9.7	-
A-23 D		3.5	28	8	25	-	8	72.5	137	3517	1239	15	500	0.90	0.78	9.0	-
A-22 P		1.0	-	3	71	136	22	233.0	62	5479	315	71	0	0.47	0.82	5.1	136
A-21 D		5.5	9	11	45	50	21	141.5	134	4029	1160	11	500	0.92	0.76	8.7	9
S-2 W		4.0	-	4	84	94	23	209.0	92	3282	592	48	0	0.66	0.74	6.4	24
S-3 P		2.5	-	-	33	102	10	147.5	66	2445	309	74	0	0.47	0.75	4.7	41
S-1 D		3.0	-	5	32	40	11	91.0	132	3800	1256	12	600	0.92	0.77	9.5	13
A-20 D		3.4	-	8	38	49	7	105.4	133	4187	1463	12	700	0.92	0.79	11.0	14
A-19 W		1.0	-	3	43	66	19	132.0	115	2585	1050	29	0	0.80	0.78	9.1	66
A-18 P		0.3	-	-	17	70	8	95.3	70	1925	567	67	200	0.51	0.80	8.1	233
A-17 W		1.0	-	-	48	77	33	159.0	135	4607	1401	17	600	0.89	0.80	10.4	77
A-16 W		1.9	-	6	33	-	4	44.9	114	5413	908	30	400	0.79	0.76	8.0	-
A-15 P		0.5	-	5	41	79	16	141.5	73	2847	477	80	0	0.48	0.78	6.5	158
A-14 D		4.6	-	10	42	45	12	113.6	138	2195	1294	11	0	0.98	0.78	9.4	10
A-13 D		2.2	-	7	29	25	-	63.2	133	2689	1161	11	0	0.92	0.80	8.7	11
M-1 W		1.8	-	-	20	74	21	116.8	114	4728	1032	23	300	0.83	0.75	9.1	41
A-12 D		2.6	-	6	36	53	12	109.6	143	4055	1236	14	0	0.91	0.77	8.6	20
A-11 D		-	-	-	44	60	5	109.0	68	2572	416	77	0	0.47	0.77	6.1	-
A-10 D		1.0	-	3	25	30	5	64.0	134	2855	1368	13	500	0.91	0.77	10.2	30
A-9 D		1.5	-	-	23	-	2	26.5	136	3501	1334	11	600	0.93	0.78	9.8	-
A-8b W		-	-	-	40	-	40	80.0	89	4995	853	38	300	0.70	0.78	9.6	-
A-8a W		1.5	-	2	30	36	12	81.5	110	2352	1056	15	600	0.88	0.76	9.6	24
A-7b P		0.1	-	-	24	-	20	44.1	72	1912	425	58	300	0.55	0.73	5.9	-
A-7a W		-	-	-	51	-	9	60.0	97	4221	1148	41	500	0.70	0.81	11.8	-
A-6 W		2.1	-	-	46	50	7	105.1	117	2118	975	24	400	0.83	0.72	8.3	24
A-5 D		2.4	-	-	35	21	4	62.4	132	2595	1143	11	0	0.92	0.78	8.7	9
A-4 D		1.1	-	4	44	44	7	100.1	127	1966	1159	13	0	0.91	0.79	9.1	40
B-1 P		2.4	-	5	106	80	23	216.4	129	4255	1195	15	400	0.90	0.78	9.3	33
B-2 P		-	-	-	-	-	6	6.0	73	2460	337	86	0	0.46	0.81	4.6	-
A-3 D		2.4	-	-	132	83	23	240.4	120	4943	1162	12	0	0.91	0.75	9.7	35
A-2 D		1.5	-	-	47	-	9	57.5	139	3446	1294	10	600	0.94	0.79	9.3	-
A-1 D		1.0	-	7	85	-	7	100.0	132	4171	1264	10	400	0.93	0.78	9.6	-

1. Above 2 $\sigma$  of background level.

- : below detection limit. In all cases, the concentrations of Os are below the detection limit (3 ppb).

\* : detection limit of the PGE, in ppb: Ir(0.1), Ru(5), Rh(1), Pt(5), Pd(5), Au(1).

RT\*\* : dunite (D), wehrlite (W), pyroxenite (P).

believe that such samples give more accurate absolute concentrations. The results are listed in Table 1. Os and Ru concentrations are under or close to detection limits and are not further used in this study. The total sulfur was determined by infrared absorption spectrometry.

## GEOCHEMISTRY

The first column of Figure 4 shows the variation of the ratio Co/(Co+Sc) in the rock types as function of stratigraphy. Cobalt (115–145 ppm) is concentrated in dunite, and scandium (60–80 ppm), in pyroxenite. Olivine-rich horizons (ORH) are characterized by a Co/(Co+Sc) value greater than 0.8, and pyroxene-rich horizons (PRH), by a value less than 0.5. The interval between these extreme values represents transitional rocks of mainly wehrlitic composition. Nickel abundance in ORH is higher than 1000 ppm, whereas the Ni content of pyroxenite varies between 300 and 500 ppm. Chromium is not a good discriminant for the pyroxenitic unit because

it is partitioned into two mineral phases, chromite and pyroxene, which are present in different proportions in wehrlite and pyroxenite. Chromite is associated with ORH. The maximum Cr value found in these rocks is 5386 ppm.

The second column of Figure 4 shows magnesium number, Mg#, as a function of stratigraphy. The Mg# shows a limited variation (0.7–0.85), but the irregular distribution suggests that several liquids were injected into the magma chamber. This interpretation is supported by the higher Mg# in pyroxenite than in dunite. The restricted range of Mg# values suggests that the various melts were not extensively differentiated.

The third column of Figure 4 shows the variation in PGE as a function of stratigraphy. The major trend seems to be controlled mainly by Pt (70–130 ppb) and Pd (75–130 ppb). Their irregular distribution is not closely related to the rock type or sulfur abundance (Fig. 4, column 4). The sulfur content is very low (0–700 ppm). The maximum gold value (40 ppb) is found in a transitional rock [Co/(Co+Sc) = 0.70, S content 300 ppm].

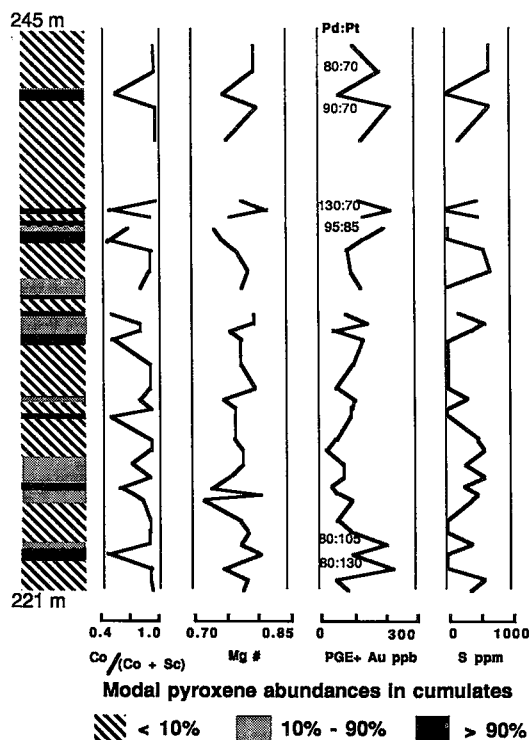


FIG. 4. Co/(Co+Sc) ratio, Mg#, PGE and S variation in the section.

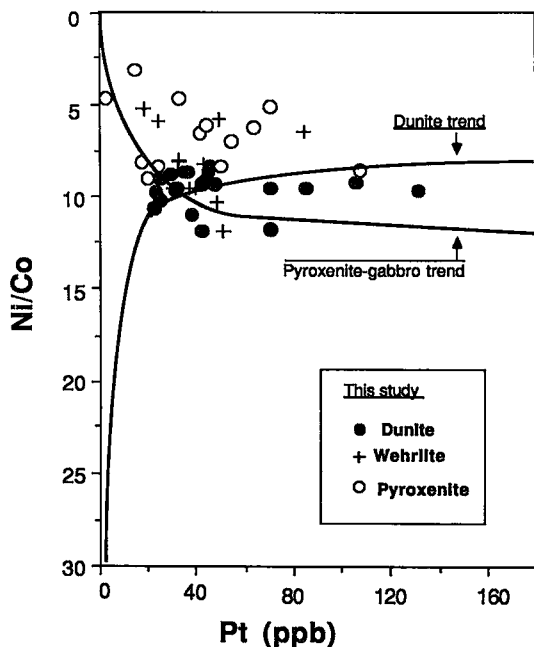


FIG. 5. Diagram of Ni/Co ratio versus Pt content in TMO (modified after Oshin & Crocket 1982). Interpreted trends are from the same authors.

## DISCUSSION

Other PGE data on the TMO (Oshin & Crocket 1982) show the same pattern of variation as the sequence above the Hall chromite orebody. Oshin & Crocket (1982) observed an overlap between chromite-dunite and pyroxenite-gabbro trends (Fig. 5). The overlap in Ni/Co suggests that many liquids were involved in the magma chamber. This contention is supported by the variable Pd/Ir values (at fixed Mg#); this ratio generally increases with advancing fractionation (Table 1; Oshin & Crocket 1987, Crocket 1981, Barnes 1987, Economou-Eliopoulos & Paraskevopoulos 1989). Pd/Ir values measured in an orthopyroxene-rich dike indicate that it is not related to the main sequence of cumulates and is derived from a different melt. Pd/Ir values in the ultramafic cumulates suggest their derivation from Mg-rich melt such as a komatiitic (Keays 1982) or a boninitic magma (Hamlyn *et al.* 1985). These liquids are likely derived from melting of different sources or by various degrees of partial melting of similar sources. The highest Pt contents are observed for a Ni/Co ratio within the range 5 to 10. This observation could be interesting as a prospecting guide for PGE since pyroxenites are better exposed than dunite and chromitite in ophiolitic complexes. Values of Pt over 80 ppb in pyroxenite having an appropriate Ni/Co value could indicate ore-grade concentrations at the base of the sequence of cumulates if underlying chromitite units do not crop out.

We must note that some discrepancies in absolute PGE content with the data of Oshin & Crocket (1982) reflect the analytical method and the total number of samples analyzed. The wider variation in total lateral PGE content at a fixed Ni/Co value established in this study is considered to result from the higher density of sampling on a statistically representative small area (Fig. 2). In addition, the study area is located near PGE-anomalous dunitic cumulates (the Hall chromite orebody). However, it is interesting to find the same overall variation in the Ni/Co values in both investigations.

The chondritic normalization of PGE reveals a positive slope and a pattern very depleted in Ir-Pd (Fig. 6). For instance, normalized values are 40 (Ir) to 20 (Pd) times lower than values measured in chromitite from the Stillwater and Bushveld layered complexes. The patterns are parallel, suggesting that major fractionation of the platinum-group elements (especially Ir) occurs along with olivine and chromite fractionation. Increase of Pd values follows an interval over which clinopyroxene was a major fractionating phase in the sequence of cumulates. Coprecipitation of both PGE alloys and sulfides with silicate phases might coincide with variable  $f(S_2)$  and low  $f(O_2)$  of the liquid. This interpretation agrees with the mineralogical assemblages documented by Cor-

rivaux & Laflamme (1989, 1990), who identified *PGE* alloys and sulfides. Figure 6 also shows that ultramafic cumulates in the TMOC display a positive slope compared to chromitite from ophiolitic complexes in Oman (Om), New Caledonia (NC) and Newfoundland (Nf) (Page & Talkington 1984), but similar to the Voikar-Syninsky ophiolite (VS), USSR (Page *et al.* 1983). This difference suggests a different pattern of fractionation or different *PGE* abundances (or both) for the cumulates of TMOC and VS. However, Pt and Pd values for the pyroxene-bearing TMOC cumulates are higher than values obtained in dunites and chromitites from Oman, New Caledonia and Newfoundland and pyroxene-bearing cumulates from Voikar-Syninsky. This finding suggests that Pt concentration in equally fractionated melts was more important in the case of the TMOC than in melts that generated other ophiolitic cumulates. This hypothesis holds if  $f(S_2)$  was low during fractionation of pyroxene-bearing cumulates. In addition, the occurrence of a potential Pt orebody immediately south of the cross-section studied, which would be unusual for an ophiolite (Crocket 1981), is in agreement with our results. Prichard & Tarkian (1988) found high Pt concentrations for chromite-bearing peridotitic cumulates in the Shetland ophiolite similar to those presented here. Interestingly, their interpretation (Prichard & Lord 1988) of a suprasubduction environment for the Shetland ophiolite, based on occurrence of boninites in the volcanic sequence, fits very well with the interpretation of Crocket & Oshin (1987), Laurent & Hébert (1989) and Hébert & Laurent (1989) for TMOC. The presence of boninites in the volcanic and hypabyssal sequences established in the Thetford Mines area is consistent with this hypothesis. There is general agreement that boninite represents the product of hydrous partial melting of upper mantle in arc systems [see Beccaluva & Serri (1988) for a review]. The generation of boninitic magma by melting of a refractory harzburgitic source suggests a similar origin for the melts that produced the TMOC cumulates. According to this model, the *PGE* could be preferentially concentrated in the source if melting occurred at low  $f(S_2)$  and then released at a stage of arc magmatism. If we compare the sulfide-solubility curve published by Naldrett & von Gruenewaldt (1989) with our data, the melts generated during arc magmatism were likely to have been undersaturated. Similar conclusions were reached by Economou-Eliopoulos & Paraskevopoulos (1989). This model is essentially similar to the scheme presented by Hamlyn *et al.* (1985). Actual *PGE* concentrations are not fully explained in terms of magmatic processes, since no satisfactory petrological model can account for the data at hand. For instance, data on intensely altered peridotites (not reported here) indicate high total *PGE* concentration not associated with signifi-

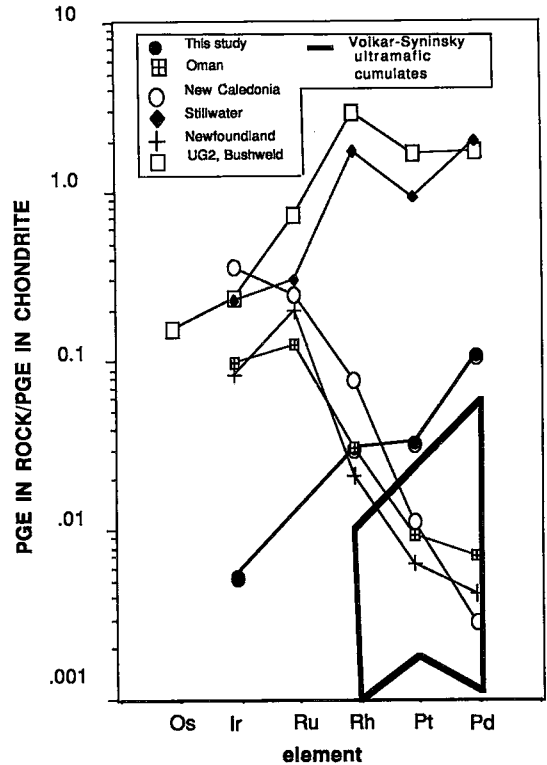


FIG. 6. Diagram of *PGE* in rock normalized to *PGE* in C1 chondrite. The lines show the average of the normalized data. Patterns for layered and ophiolitic complexes are taken from Page & Talkington (1984).

cant S contents. Hydrothermal circulation is believed to play a role in mobilization of *PGE* from their initial sites of deposition. Intense serpentinization and amphibolitization are processes possibly responsible for this secondary mobilization (work in progress).

#### CONCLUSIONS

Observations of cross-cutting orthopyroxene-rich dikes, the irregular variations of Mg#, and the overlapping Ni/Co values for pyroxenitic and dunitic trends suggest that several melts were involved in the formation of the sequence of cumulates of the TMOC. However, restricted variation in Mg# suggests that these magmas had similar Mg/Fe values. The actual distribution of *PGE* is explained in two steps: 1) magmatic and, tentatively, 2) hydrothermal. The fractionation of *PGM* occurred at different Ni/Co values, between 5 to 10, regardless of stratigraphy and rock type. The *PGE* were possibly reworked during several stages of hydrothermal alter-

ation that affected mainly the base of the sequence of cumulates. Pyroxenitic cumulates could be good indicators of local PGE concentration in the generally poorly exposed underlying olivine- and chromite-rich cumulates. These preliminary results are in agreement with an origin of the TMOC in an arc environment, where multistage melting of a refractory mantle source is needed to explain both high PGE contents and the occurrence of boninite.

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