

TRENDS IN THE DISTRIBUTION OF THE PRECIOUS METALS IN THE LAC-DES-ILES COMPLEX, NORTHWESTERN ONTARIO

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ABSTRACT

The Archean Lac-des-Iles complex, located in north-western Ontario, is a sulfide-bearing layered mafic-ultramafic body. The magmatic sulfide and platinum-group element (PGE) mineralization is commonly associated with mafic cumulates. Later geological processes involving a fluid phase, however, have altered primary silicates, redistributed the Cu-Ni sulfides and produced PGE-bearing tellurides, arsenides, bismuthotellurides and sulfides. In several PGE-bearing samples, secondary violarite-siegenite, sphalerite, galena and clausthalite have been identified. Whole-rock chemical compositions demonstrate that a strong relative enrichment of (Pt + Pd), in most cases, occurs at low Cu, Ni and Au concentrations. The ratios Cu/(Cu + Ni) and Pt/(Pt + Pd) are highly variable even if mineral alteration and lithological groupings are considered. The geochemical data indicate that hydrothermal processes are active in the mobilization and concentration of the precious metals, inasmuch as: (1) most PGE minerals are associated with secondary sulfides and silicates, even where the pyroxene and plagioclase are not totally altered, and (2) the highest PGE values are associated with once pyroxene-rich rocks, now predominantly composed of amphiboles.

Keywords: Lac-des-Iles, sulfide, platinum-group element, redistribution, hydrothermal processes, Ontario.

SOMMAIRE

Le complexe stratiforme archéen du lac-des-Iles, situé dans le Nord-Ouest de l'Ontario, se caractérise par des roches mafiques et ultramafiques minéralisées en sulfures. La minéralisation en éléments du groupe du platine (EGP) et en sulfures magmatiques est généralement associée aux cumulats mafiques. Des processus géologiques ultérieurs impliquant une phase fluide ont cependant altéré les silicates primaires, redistribué les sulfures de Cu-Ni et produit des tellurures, arséniures, bismuthotellurures et sulfures porteurs d'EGP. On a identifié la violarite-siegenite, la sphalérite, la galène et la clausthalite comme phases secondaires dans plusieurs échantillons porteurs d'EGP. La composition chimique des roches établit, dans la plupart des cas, qu'un fort enrichissement relatif en Pt + Pd va de pair avec de faibles concentrations en Cu, Ni et Au. Les rap-

ports Cu/(Cu + Ni) et Pt/(Pt + Pd) varient fortement, même après regroupement des types d'altération minéralogique et lithologique. Les données géochimiques indiquent que les processus hydrothermaux sont actifs dans la mobilisation et la concentration des métaux précieux. En effet: (1) la plupart des minéraux à EGP co-existent avec les sulfures et silicates secondaires, même où pyroxène et plagioclase ne sont pas complètement altérés, et (2) les plus fortes valeurs en EGP sont associées à des roches originellement riches en pyroxène, où dominent maintenant les amphiboles.

(Traduit par la Rédaction)

Mots-clés: Lac-des-Iles, sulfures, éléments du groupe du platine, redistribution, processus hydrothermaux, Ontario.

INTRODUCTION

Although the results of many studies (*cf.* review by Naldrett 1981) have proven that the collection of platinum-group elements (PGE) by an early- or late-magmatic sulfide liquid is an operative mechanism, several investigations (*e.g.*, Mihalik *et al.* 1974, Stumpfl 1974, McCallum *et al.* 1976, Watkinson & Dunning 1979, Schiffrics 1982) have shown that late magmatic (deuteric) and metamorphic processes can significantly redistribute and concentrate the PGE. Magmatic and late-stage processes of concentration of the PGE are exemplified in the Lac-des-Iles (LDI) Complex. Watkinson (1975), Watkinson & Dunning (1979) and Dunning *et al.* (1981) have shown that the Cu-Ni sulfide and PGE mineralization in the LDI Complex formed from a sulfide liquid that crystallized as monosulfide solid solution (MSS) which, upon cooling, exsolved most (if not all) of its contained PGE. These and subsequent studies (Watkinson 1981), however, indicate that during late-stage, deuteric-type alteration (autometasomatism) and possibly greenschist-facies metamorphism, the PGE, Cu, Ni and S are redistributed and concentrated, and overprint magmatic geochemical trends. The purpose of this paper is to show how secondary processes have geochemically modified magmatic PGE trends in the Lac-des-Iles Complex.

GENERAL GEOLOGY

The Lac-des-Iles Complex is located approximate-

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Publication 13-83 of the Ottawa-Carleton Centre for Geoscience Studies.

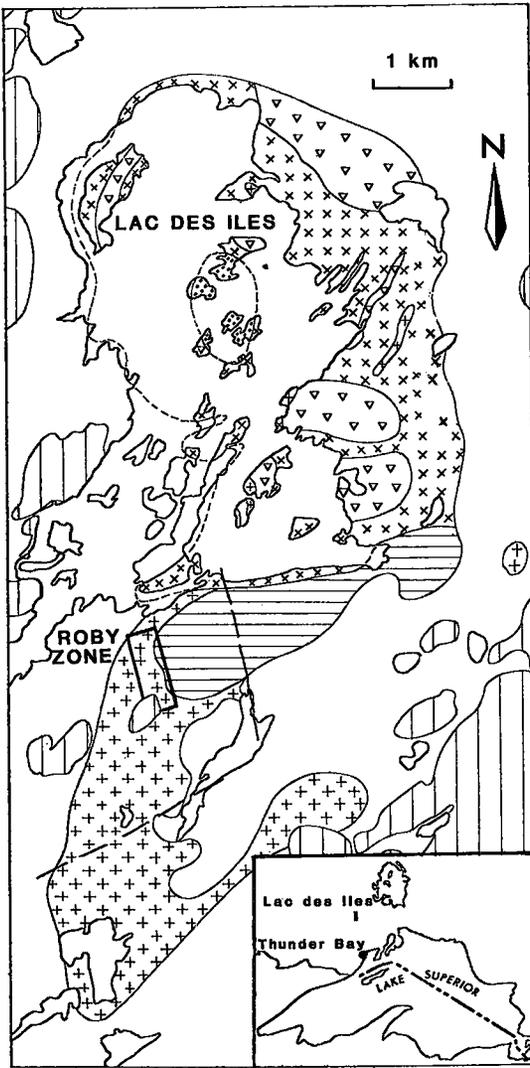


FIG. 1. Geology of the Lac-des-Iles complex showing the location of the Roby zone (after Texasgulf Canada, Ltd.). Legend: + western gabbro, horizontal ruling eastern gabbro, x pyroxenite, ∇ peridotite, dots websterite; area without a pattern: granitoid rocks; vertically ruled area: Keweenaw diabase.

ly 80 km NNW of Thunder Bay, Ontario (Fig. 1). It is intruded into Archean granitoid and gneissic rocks of the Wabigoon belt (Pye 1968) and cut by granitoid rocks emplaced during the Kenoran event, and sills and dykes of Keweenaw-type diabase. Even though many of the LDI rocks retain their primary textures and mineralogy, they have been mildly to moderately deformed and metamorphosed to the greenschist or lower amphibolite facies dur-

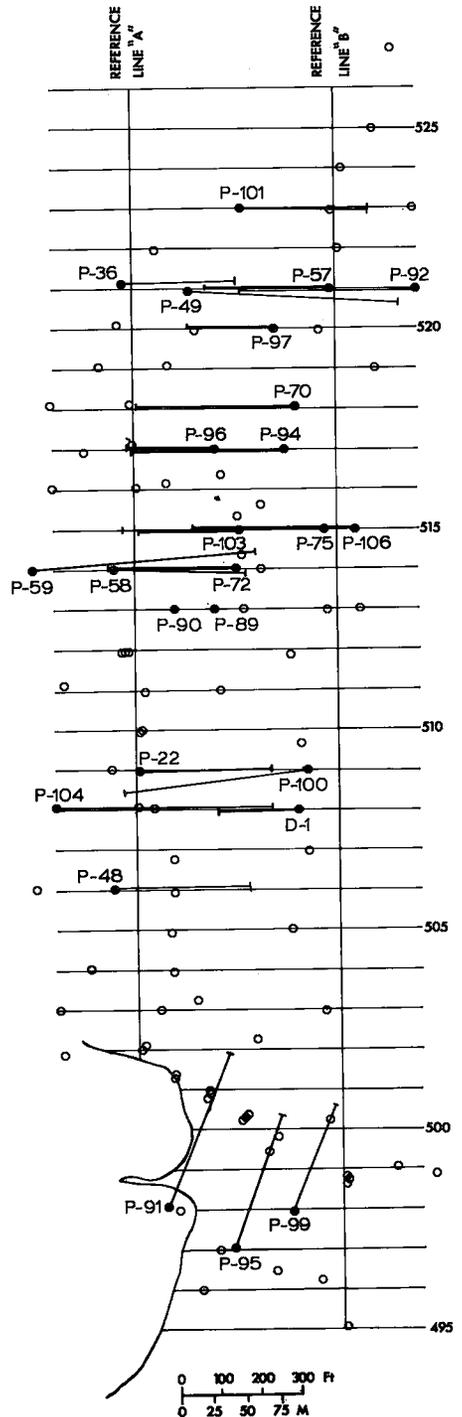


FIG. 2. Locations of diamond drill-holes studied in the Roby zone (after Texasgulf Canada, Ltd.).

ing the Kenoran event (Pye 1968, Watkinson & Dunning 1979). The complex is divided into three intrusive units: (1) the western gabbro, (2) the eastern gabbro and (3) the ultramafic zone. The western gabbro contains all of the known significant PGE mineralization (mostly in the Roby zone: Fig. 2) and consists of interlayered cumulates of gabbroic (70%), noritic (20%), pyroxenitic (10%) and minor anorthositic rocks (Watkinson & Dunning 1979). From west to east in the Roby zone, these rocks are plagioclase, plagioclase-orthopyroxene and clinopyroxene cumulates.

SULFIDES AND PLATINUM-GROUP MINERALS

Watkinson (1975) made a preliminary study of the mineralogy and petrology of drill-core and surface samples, and recognized assemblages of primary and secondary sulfides and platinum-group minerals (PGM). Cabri & Laflamme (1979) studied sulfide and PGM concentrates from some rocks with high assays of the PGE. The principal PGM are braggite, vysotskite, kotulskite, isomertieite, merenskyite, sperrylite, moncheite, stillwaterite, palladoarsenide and an unnamed mineral with a formula of Pd_5As_2 .

The sulfides present in the PGE zone (Roby zone) at LDI are, in order of decreasing abundance, pyrite, chalcopyrite, pentlandite, pyrrhotite, millerite, violarite, sphalerite and galena (Dunning 1979). Sulfides occur as disseminated blebs in all rock types; in some noritic and anorthositic rocks they are net-textured. Dunning (1979) also recognized the follow-

ing assemblages, all with chalcopyrite, in the mineralized Roby zone: 1) pyrrhotite-pentlandite-pyrite, 2) pyrrhotite-pyrite, 3) pentlandite-pyrite, 4) pentlandite-millerite-violarite, 5) pentlandite-millerite, 6) pyrite-millerite and 7) pyrite. The first three assemblages represent a slightly metamorphosed equivalent of primary exsolution from MSS and occur in most net-textured sulfide-bearing rocks. Assemblages 4 to 6 occur in altered gabbroic rocks and are interpreted to be metamorphosed assemblages of oxidized equivalents of assemblages 1 to 3. Assemblage 7 is locally abundant in shear zones as stringer sulfide or massive sulfides. PGM and Au occur with most of these assemblages (Table 1).

Dunning (1979) and Watkinson & Dunning (1979) have reported that the noritic layers contain the highest concentrations of PGE (maximum 16.6 ppm total PGE + Au for unaltered lithologies). There is also a rough association of PGE with pyroxene cumulates. Sheared and altered gabbroic and clinopyroxenitic lithologies contain the highest (though variable) concentrations of PGE. The high concentration of PGE in altered rocks, especially pyroxene cumulates, is probably related to mobilization, predominantly of Pd and Au (Watkinson & Dunning 1979).

Recently, Dunning *et al.* (1981) presented whole-rock geochemical data for 3-metre sections of drill core, from which they examined PGE + Au *versus* Cu and Ni for various lithologies of the complex. Their results indicate that for noritic rocks, two

TABLE 1. PLATINUM-GROUP MINERAL, SULFIDE AND SILICATE ASSEMBLAGES IN PGM-BEARING SAMPLES

Sample	Rock Type ¹	Plagioclase Alteration	Mineral Assemblage
P22-353.3-5	I	100	1. vysotskite (actinolite+chlorite) 2. palladoarsenide (actinolite+chlorite)
P55-58.0-6	I	100	braggite+cp+po (amphibole+sericite)
P55-60.3-5	I	100	1. kotulskite+cp (actinolite) 2. vysotskite+cp+po (chlorite+sericite+epidote alteration of plagioclase)
P55-103.2-1	I	100	braggite+po+sph (actinolite+chlorite)
P75-394.4-3	I	100	1. palladoarsenide+cp (chlorite + hornblende?) 2. palladoarsenide (actinolite)
P97-260	I	100	vysotskite+cp+pn+mi (chlorite + talc)
P55-55.0-2	II	30	kotulskite+cp (hornblende)
P97-193.0-1	II	50	kotulskite+pn-py (actinolite+chlorite)
P67-149.0-0	III	5	vysotskite+cp+py+mt (incipient talc alteration of orthopyroxene)
P55-10.0-2	VII	50	kotulskite+cp (sericitized plagioclase)

¹ I amphibolite, II augite norite, III norite, IV bronzite gabbro, V felsic gabbro, VI anorthosite - felsic gabbro, VII gabbro (classification after Dunning 1979). Mineral abbreviations: cp chalcopyrite, py pyrrhotite, sph sphalerite, pn pentlandite, mi millerite, py pyrite, mt magnetite.

geochemical trends, magmatic and secondary, are discernible (see below, Figs. 6, 7). No statistical trend is evident for strongly altered gabbroic and clinopyroxenitic lithologies.

Naldrett (1981) reported an averaged composition of 25 samples of "typical ore" from the Roby zone: 0.172% Ni, 0.128% Cu, 0.32% S, 0.9 ppm Pt, 16 ppm Pd, 0.011 ppm Rh, 0.003 ppm Ru, 0.0004 ppm Ir, 0.0002 ppm Os and 0.68 ppm Au.

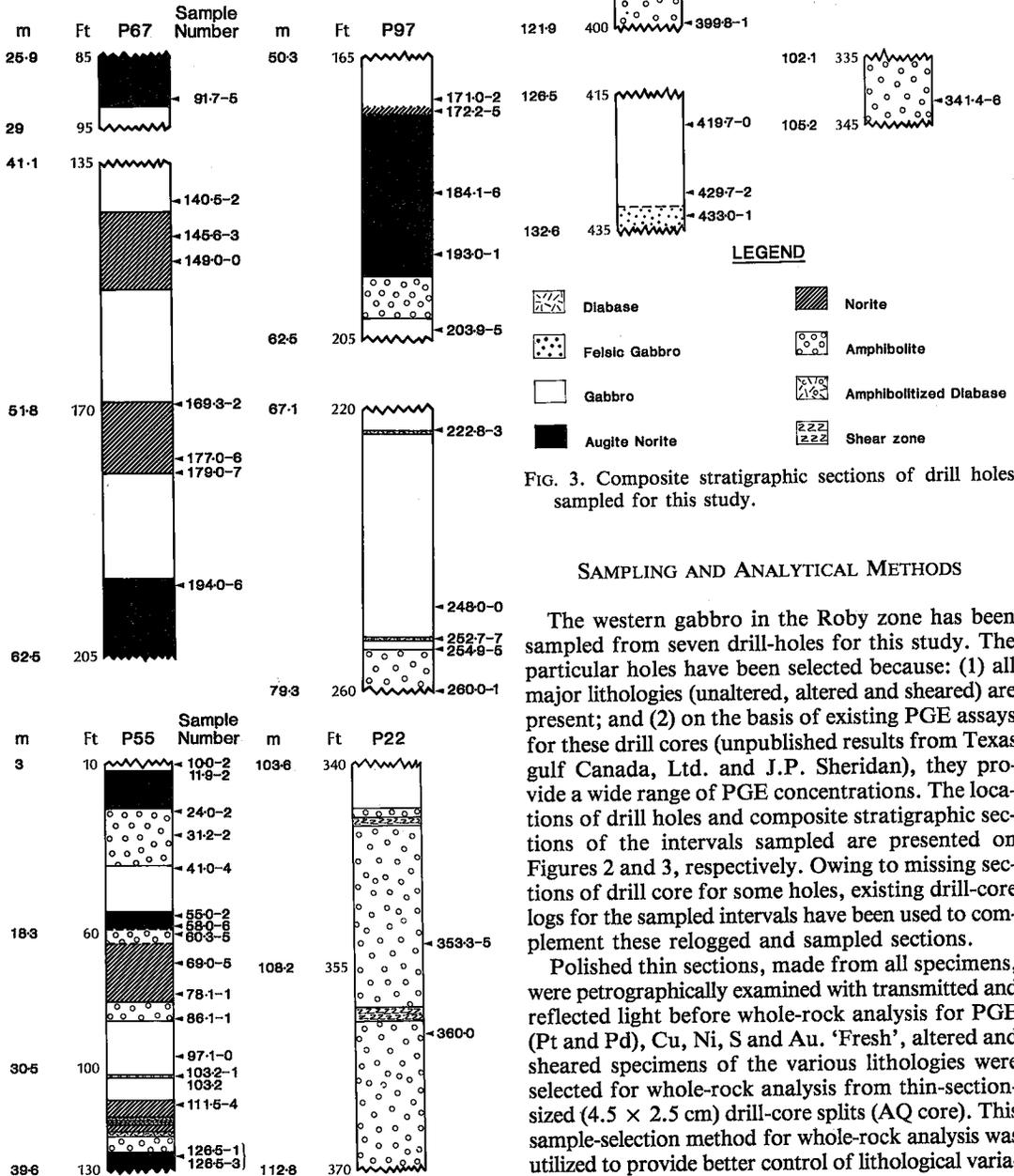


FIG. 3. Composite stratigraphic sections of drill holes sampled for this study.

SAMPLING AND ANALYTICAL METHODS

The western gabbro in the Roby zone has been sampled from seven drill-holes for this study. The particular holes have been selected because: (1) all major lithologies (unaltered, altered and sheared) are present; and (2) on the basis of existing PGE assays for these drill cores (unpublished results from Texas Gulf Canada, Ltd. and J.P. Sheridan), they provide a wide range of PGE concentrations. The locations of drill holes and composite stratigraphic sections of the intervals sampled are presented on Figures 2 and 3, respectively. Owing to missing sections of drill core for some holes, existing drill-core logs for the sampled intervals have been used to complement these relogged and sampled sections.

Polished thin sections, made from all specimens, were petrographically examined with transmitted and reflected light before whole-rock analysis for PGE (Pt and Pd), Cu, Ni, S and Au. 'Fresh', altered and sheared specimens of the various lithologies were selected for whole-rock analysis from thin-section-sized (4.5 x 2.5 cm) drill-core splits (AQ core). This sample-selection method for whole-rock analysis was utilized to provide better control of lithological varia-

tions, alteration and mineralization and to evaluate the previously recognized correlation of PGE with lithologies of the western gabbro in assays of 3-metre sections of drill core.

Pt, Pd and Au analyses were performed by a fire-assay atomic absorption method by Bondar-Clegg and Company, Ltd., Ottawa. A sample weight of 10 g and approximately 2.5 mg of Ag are used for the preparation of Doré beads (PGE + Au preconcentration step) prior to acid digestion. Detection limits for Pt, Pd and Au, as reported by Bondar-Clegg, are 15, 2 and 15 ppb, respectively. Cu and Ni were determined by atomic absorption. The detection limits for Cu and Ni are 1 and 2 ppm, respectively. Total S was determined by X-ray fluorescence using a 5 g sample. The detection limit is 20 ppm.

Sample 5 was halved and run as two unknown samples. The analytical results show only minor differences (in %) in absolute abundances: Cu(0), S(0), Ni(~7), Pt(~7), and Au(~13), except Pd where there is an order of magnitude difference (~1000 *versus* ~16,000). This difference in Pd may be caused by several factors, such as an uneven distribution of palladium minerals in each split, their small size (~50 µm) and trace modal abundances.

RESULTS

Petrography of PGM-bearing samples

Complete petrographic descriptions and mineral compositions of silicates and opaque phases for all rock types of the western gabbro are presented by Watkinson (1975), Cabri & Laflamme (1979) and Dunning (1979). Briefly, Watkinson (1975) and Dunning (1979) recognized primary and secondary sulfide-PGM assemblages. These can be distinguished on the basis of the presence of disseminated grains of pyrite and chalcopyrite (\pm PGM) in secondary silicates (*e.g.*, amphibole and chlorite) and trains of pyrite porphyroblasts within fractures emanating from sulfide blebs. Sulfide assemblages that contain millerite, violarite, sphalerite or galena are also interpreted as secondary. Although Dunning's (1979) work shows that there is a distinction between assemblages of primary and secondary sulfides, his distinction between assemblages of deuteric and metamorphic sulfides is less clear for several reasons: 1) the paucity of equilibrium microstructures (*e.g.*, triple-point junctions, *etc.*), 2) the presence of pervasive alteration in most specimens of all lithologies and in primary mineral phases, 3) the lack of penetrative deformation, except locally in shear zones, and 4) the presence of gabbroic pegmatites. These features suggest that deuteric alteration was, at least locally, more effective than any subsequent metamorphic event.

PGM have been identified in ten specimens

examined during this study. Of these specimens, six are amphibolites whose precursor could not be determined owing to extensive alteration of primary silicate phases; two are augite norite (Dunning 1979) and one each of gabbro and norite. The PGM and associated minerals are listed in Table 1. In several of the PGM-bearing samples, violarite-siegenite, sphalerite, galena and clausthalite have also been identified. These minerals have been shown to be nonprimary in this environment (Craig 1971, Hudson & Groves 1974, Mihalik *et al.* 1974, Watkinson 1975).

Photomicrographs of some of the typical PGM-sulfide-silicate assemblages are shown on Figure 4. Incipient alteration of orthopyroxene to talc and oxidation of primary intercumulus sulfide are developed in a weakly altered norite (Fig. 4A), whereas in a nearly totally altered gabbro, a circular grain of kotulskite in ragged chalcopyrite occurs in sericitized plagioclase (Fig. 4B). A variety of assemblages occurs in amphibolite (Figs. 4C-F). Occasionally, discrete PGM occur in altered primary silicates (Fig. 4C). However, the PGM are more commonly associated with other sulfides, but always occur with altered primary silicates.

The petrographic data for LDI indicate that six out of ten PGM occur in amphibolite as sulfides, arsenides and bismuthotellurides (Tables 1, 2). Other PGM-bearing samples are augite norite, norite and gabbro. In all cases except norite, the PGM are associated with either secondary amphibole or altered plagioclase. In the norite, the PGM are associated with orthopyroxene, which has been slightly altered to talc.

Whole-rock geochemistry

The whole-rock geochemical data for the 18 analyzed rock samples are listed in Table 3 and grouped according to rock type in Table 4. Although amphibolite, augite norite and bronzite gabbro have the highest contents of total PGE, the statistical results show that, in the case of amphibolite and augite norite, the variance is high. Norite has low total PGE, 3.66 ppm, and high variance. In an attempt to determine the cause of the high statistical variance in PGE, modal content of sulfide and extent of alteration of pyroxene have been examined.

The sulfide content of the LDI rocks is variable, though commonly less than 1 modal % (Table 5), and does not appear to correlate with either the whole rock Cu/(Cu + Ni) ratio (Table 5) or the PGE content. However, three analyzed amphibolites (samples 1, 5, 18) contain high S and (Pd + Pt) contents. Sample 2 (Table 5) has a high Cu/(Cu + Ni) ratio and sulfide content with a moderately high (Pt + Pd) content.

Even though a name referring to an unaltered rock

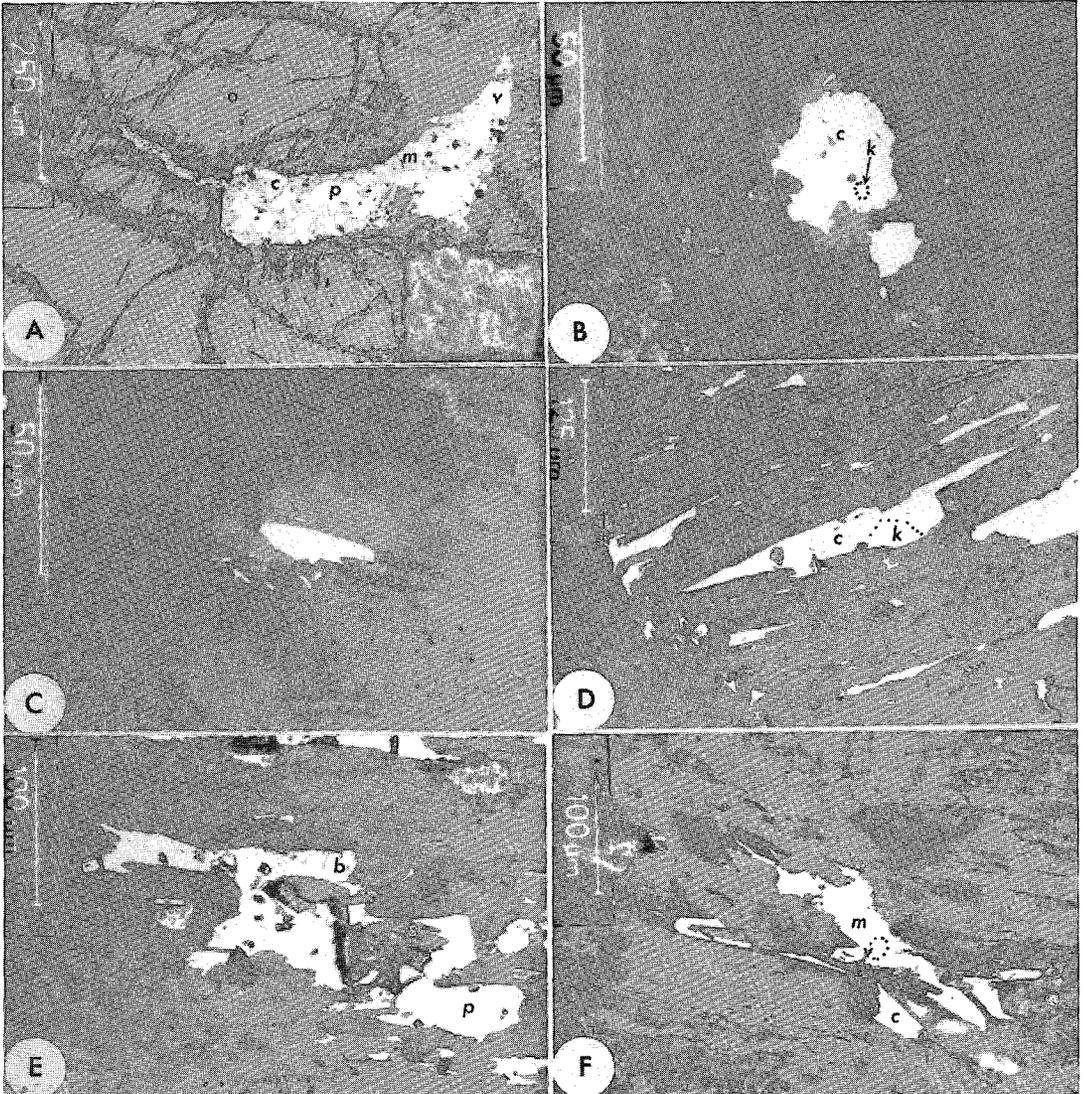


FIG. 4. Photomicrographs taken in plane-polarized reflected light. A. Partially oxidized assemblages of primary sulfides in norite: orthopyroxene (o), talc (t), chalcopyrite (c), pyrite (p), magnetite (m), vysotskite (v). Sample P67-149.0-0-1. B. Single grain of kotulskite (k) in ragged chalcopyrite (c) in sericitized plagioclase in gabbro. Sample P55-10.0-2-4. C. Solitary grain of palladoarsenide in secondary amphibole in amphibolite. Sample P75-394.4-3-1. D. Kotulskite (k) grain in chalcopyrite (c) along cleavage planes in secondary amphibole in amphibolite. Sample P55-60.3-5-4. E. Braggite (b) + pyrrhotite (p) + sphalerite (s) in secondary amphibole and chlorite in amphibolite. Sample P55-103.2-1-3. F. Vysotskite (v) + chalcopyrite (c) + millerite (m) in secondary amphibole; amphibolite sample P97-260-1.

has been assigned to most of the samples in this study, most have been altered to varying degrees. The pyroxenes are commonly altered to assemblages of actinolite \pm talc \pm chlorite \pm hornblende \pm magnetite \pm biotite \pm carbonate. Plagioclase alteration to sericite \pm epidote \pm chlorite \pm carbonate

is less extensive than pyroxene alteration. The status of alteration of the pyroxenes in the different rock types is listed in Table 5. In amphibolite, all pyroxenes are 100% altered.

Norite shows no consistent geochemical trend for Pt and Pd with progressive alteration of pyroxene,

TABLE 2. NEW ELECTRON-MICROPROBE DATA ON PLATINUM-GROUP MINERALS, LAC-DES-ILES COMPLEX

	1	2	3	4	5	6	7
Pd	36.0	43.3	64.1	70.8	44.8	42.8	43.2
Pt	41.1	31.4	0.98	3.30	0.29	0.40	0.24
Te	-	n.d.	0.04	-	52.1	51.8	50.6
Bi	-	2.96	0.60	-	4.89	3.28	4.76
S	19.1	19.2	21.4	22.79	0.08	-	0.08
Ni	4.00	3.60	6.35	0.82	0.04	0.03	0.10
Pb	-	n.d.	n.d.	-	0.49	1.15	1.26
As	n.d.	-	-	0.07	-	-	-
Fe	-	-	-	2.97	-	-	-
Sb	-	-	-	-	-	-	-
TOTAL	100.20	100.46	93.47	100.75	102.69	99.46	100.24

- not determined, n.d. not detected. Mineral abbreviations: cp chalcopyrite, po pyrrhotite, sph sphalerite, pn pentlandite, py pyrite, mt magnetite.

1. Braggite (Pd₅₅Pt₃₄Ni₁₁)S₉₇ + cp + po in amphibole and sericite; amphibolite; sample P55-58.0-6-2.
2. Braggite (Pd₆₅Pt₂₆Ni₉) (Bi_{0.02}Fe_{0.98}) + pn + sph + cp in amphibole and chlorite; amphibolite; sample P55-103.1-3.
3. Vysotakite (Pd₈₄Pt₀₁Ni₁₅) S₁₀₇ + cp + po in chlorite, sericite, epidote alteration of plagioclase; amphibolite; sample P55-60.3-2.
4. Vysotakite (Pd₈₉Pt₀₁Ni₁₀Fe_{0.8}) S₉₅ + cp + py + mt in talc alteration of orthopyroxene; norite; sample P67-149.0-0.
5. Kotulskite (Pd₁₀) (Te₉₇Bi_{0.05}Pb_{0.1})₁₀₃ + cp in amphibole; amphibolite; sample P55-60.3-4.
6. Kotulskite (Pd₉₉Pt₀₁) (Fe_{1.01}Bi_{0.05}Pb_{0.1})₁₀₆ + cp in amphibole; augite norite; sample P55-55.0-2.
7. Kotulskite (Pd₁₀) (Te₉₇Bi_{0.05}Pb_{0.1})₁₀₄ + pn + py in amphibole and chlorite; augite norite; sample P97-193.04-4.

whereas Au shows a sympathetic increase with pyroxene alteration (0-40%). For augite norite, the absolute abundances of Pt, Pd and Au increase with increasing alteration of pyroxene (10 to 100%). This relationship is consistent with the occurrence of kotulskite in secondary amphibole and with data on PGM + sulfide + silicate assemblages (Tables 1, 2).

The amphibolite data show wide variability of Pt, Pd and Au among the four samples. A comparison of these values with the two augite norite samples, in which the pyroxenes are 100% altered, reveals a high correlation of PGE content with pyroxene alteration, but also with whole-rock alteration. Pd and Au show the highest correlation with extent of alteration (Table 5).

A composite chondrite-normalized (CN) PGE plot for unaltered lithologies is shown in Figure 5. The CN data for norite and augite norite are their mean values. The most striking feature is that for all lithologies, the PGE abundance relationship is Pd > Au > Pt. Bronzite gabbro, with a ratio orthopyroxene (opx)/[orthopyroxene + clinopyroxene (cpx)] in the range 26-50, and augite norite, in the range 51-75 (cf. Dunning 1979), have similar CN patterns. However, as the ratio opx/(opx + cpx) increases for all LDI rocks, the relative abundances of the PGE decrease except for anorthosite - felsic gabbro and felsic gabbro. For these rock types, the pyroxenes are totally altered, and the rocks have low total PGE (Table 3). Where we have found a range from 0 to 100% in degree of pyroxene alteration for a lithology, i.e., augite norite, the PGE content increases with pyroxene alteration. The limited data for the other lithologies preclude further conclusions.

In order to establish if there is a correlation between Pt + Pd and Cu, Ni and Au, as has been established by Dunning (1979) and Dunning *et al.* (1981), the new LDI data have been plotted on varia-

TABLE 3. WHOLE-ROCK GEOCHEMICAL RESULTS FOR SELECTED DRILL-CORE SAMPLES

Sample	Rock Type ¹	ppm			ppb			ppm		
		Cu	Ni	% S	Pt	Pd	Au	Pt/(Pt+Pd)	Pt+Pd+Au	Cu/(Cu+Ni)
P22-353.3-3(1)	I	12	375	0.01	110	3440	20	.031	3.57	.031
P22-360.0-14(2)	I	1900	600	4.62	345	8190	640	.040	9.18	.760
P55-55.0-2(3)	II	2400	3100	1.66	985	17900	1390	.052	20.3	.436
P55-58.0-6(4)	II	4700	3800	2.26	1185	19900	1990	.056	23.1	.553
P55-60.3-5(5)	I	3650	3500	1.73	995	15910	1640	.059	18.5	.510
P55-111.5-2(6)	III	1850	1500	1.06	360	5760	640	.059	6.76	.552
P55-111.5-5(7)	III	4940	325	1.98	15	35	70	0.300	0.12	.938
P55-128.5-1(8)	II	172	120	0.06	25	205	30	.109	0.26	.589
P57-160.0(9)	III	46	78	0.02	105	445	20	.191	0.57	.371
P57-259.5(10)	IV	445	300	0.18	300	15950	465	.018	16.7	.597
P57-260.4-260.10(11)	III	66	119	0.03	85	7940	45	.011	8.07	.357
P57-270.2(12)	III	14	48	0.02	15	95	10	0.136	0.12	.226
P67-145.6-3(13)	III	93	146	0.13	95	3580	50	.026	3.73	.389
P67-149.0-0(14)	III	58	155	0.04	130	6690	80	.019	6.90	.272
P68-291.5-5(15)	II	68	200	0.04	240	10880	140	.022	11.3	.254
P75-378.7-4(16)	V	60	105	0.08	15	150	10	.091	0.18	.364
P75-381.4-4(17)	VI	300	190	0.12	50	470	40	.096	0.56	.612
P75-399.8-1(18)	I	5530	4250	1.47	635	17400	4075	.035	22.1	.565

¹ I amphibolite, II augite norite, III norite, IV bronzite gabbro, V felsic gabbro, VI anorthosite-felsic gabbro, VII gabbro (classification after Dunning 1979).

TABLE 4. WHOLE-ROCK PGE AND Cu/(Cu+Ni) VALUES BY ROCK TYPE, IAC-DES-ILES COMPLEX

	ppb		Au	Pt/	Cu/
	Pt	Pd		(Pt+Pd)	(Cu+Ni)
AMPHIBOLITE n = 4					
mean	521	11235	1594	.044	.466
standard deviation	382	6580	1784	.012	.310
NORITE n = 7					
mean	155	3506	131	.042	.444
standard deviation	116	3365	226	.075	.241
AUGITE NORITE n = 4					
mean	609	12221	888	.047	.458
standard deviation	563	8896	960	.036	.151
BRONZITE GABBRO	300	15950	465	.018	.403
ANORTHOBSITE-FELSIC GABBRO	50	470	40	.096	.388
FELSIC GABBRO	15	150	10	.091	.036

Samples with values less than the detection limit are not used in the calculation

tion diagrams. PGE vs. Cu and Ni are plotted in Figures 6 and 7, respectively. Dunning *et al.* (1981) have shown, based on assays for 3-metre lengths, that in the noritic and gabbroic lithologies of LDI there are two geochemical trends, a primary magmatic trend, line A of Figures 6 and 7, and a trend of secondary concentration (line B). In the present study, in which petrographic control of mineral alteration was carefully monitored, there is one well-defined trend that coincides with line B of Dunning *et al.* (1981). The most striking feature of these trends is that they define similar, yet opposite, trends to those of Dunning *et al.* (1981). That is, for the gabbroic rocks in which the pyroxenes are less than 30% altered, the data fall on trend B, whereas samples

that have pyroxenes altered to more than 30% plot away from line B onto the main part of the diagram. Clearly, one cannot rely on analytical data from 3-metre sections of drill core at LDI to make critical arguments about primary and secondary distribution of the PGE.

The amphibolites plot randomly on both figures. This scatter may be an artifact of the PGE content of the unaltered precursor or a secondary enrichment in PGE during metamorphism or deuteric alteration.

The Cu/(Cu + Ni) versus Pt/(Pt + Pd) ratios of the LDI rocks have been plotted in a further attempt to determine if a correlation exists between Cu-Ni sulfides and PGE (Fig. 8). No correlation is apparent even if pyroxene alteration and lithological groupings are considered.

SUMMARY

The geochemical data for LDI indicate that hydrothermal processes for the mobilization and concentration of PGE are more common than previously recognized. Several features at LDI lead to the following conclusions: (1) The highest PGE values, though variable, are associated with amphibolites. The variability is probably the result of the "availability" of the PGE either from the unaltered precursor or from adjacent lithologies. (2) Most

TABLE 5. WHOLE-ROCK CHONDRITE-NORMALIZED PGE CONTENT AND PYROXENE ALTERATION, GROUPED BY ROCK TYPE

Sample Number ^a	Rock Type	Pt ^b	Pd ^b	Au ^b	Cu/(Cu+Ni)	Pyroxene Alteration	Modal % Sulfide
1	amphibolite	.108	6.31	.132	.031	100%	<1
2	amphibolite	.338	15.03	4.21	.760	100%	5
5 ^c	amphibolite	.975	29.19	10.79	.510	100%	tr
18	amphibolite	.623	31.93	26.81	.565	100%	1
9	norite	.103	.817	.132	.371	unaltered	--
11	norite	.083	14.57	.296	.357	unaltered	--
12	norite	<.015	.174	.066	.226	10%	1
13	norite	.093	6.57	.329	.389	10%	tr
14	norite	.127	12.28	.526	.272	10%	<1
7 ^d	norite	<.015	.067	.460	.938	40%	tr
6 ^d	norite	.353	10.57	4.21	.552	40%	tr
8	augite norite	.025	.376	.197	.589	10%	<1
15	augite norite	.235	19.96	.921	.254	30%	tr
3	augite norite	.966	32.84	9.14	.436	100%	tr
4	augite norite	1.16	36.51	13.09	.553	100%	2
10	bronzite gabbro	.294	29.27	3.06	.597	unaltered	1
17	anorthosite-felsic gabbro	.049	.862	.263	.612	100%	2
16	felsic gabbro	.015	.275	.066	.364	100%	1

a see Table 3 for corresponding drill hole and sample depth. ^b Chondrite-normalized values. The values for the CI chondrite (Pt 1020, Pd 545, Au 152, in ppb) are taken from Naldrett *et al.* (1980, p. 177, Table 1). ^c Original lithology is believed to have been augite norite. ^d Sample 7 is the fine-grained equivalent of sample 6. tr trace, -- no sulfide.

PGM are associated with secondary sulfides and silicate phases, even where the pyroxene or plagioclase of the rock is not totally altered. (3) For fresh and altered lithologies, the PGE have an abundance relationship $Pd > Au > Pt$. This is probably an artifact of primary magmatic processes that has been maintained and enhanced by secondary processes, as indicated by the PGE data for augite norite.

Cu, Ni and S show very little correlation with Pt, Pd and Au in all lithologies examined, regardless of the extent of whole-rock and pyroxene alteration, although there may be "overall" or averaged geochemical trends (*i.e.*, primary magmatic and secondary) if assay data for 3-metre sections of drill core (that may include two or more different lithologies) are considered.

Model for PGE concentration in the Lac-des-Iles complex

The western gabbroic magma was emplaced into granitoid rocks; crystallization proceeded by formation of plagioclase cumulates (dominant) followed by orthopyroxene plus plagioclase cumulates (Fig. 9). We suggest that the magma became saturated with sulfur, perhaps when the activity of FeO in the magma decreased as pyroxenes precipitated in abundance. An immiscible sulfide liquid also began to accumulate interstitially to the pyroxene-rich cumulates during this event. Since little accumulation of mafic minerals had occurred, little Ni (or precious metals) was camouflaged in early cumulus phases. Sulfide concentrations for LDI have moderate PGE contents, and their distribution tends to correlate roughly with the abundance of pyroxene cumulates.

At approximately this time, the magma became saturated with respect to a fluid phase; coarse-grained and pegmatitic textures are common in these rocks. Oxidation of Fe in the magma by fluids may have triggered the immiscibility of a sulfide liquid by decreasing the solubility of sulfur. Filter pressing of intercumulus liquid permitted fluids to percolate upward through the mush of crystals, causing extensive deuteric alteration of primary silicate cumulates. Magmatic sulfides are similarly altered and oxidized, and metallic elements such as Fe, Cu, Au and Pd have been extensively redistributed (*cf.* Stumpfl 1974, McCallum *et al.* 1976).

It is possible that the mobilization of fluid through the accumulating pile could well have been triggered by the invading eastern gabbroic liquid. Later emplacement of the ultramafic cumulates and Kenoran tectonic events, shearing and regional metamorphism may have also contributed to the present distribution of precious metals, but in our interpretation, deuteric processes predominated.

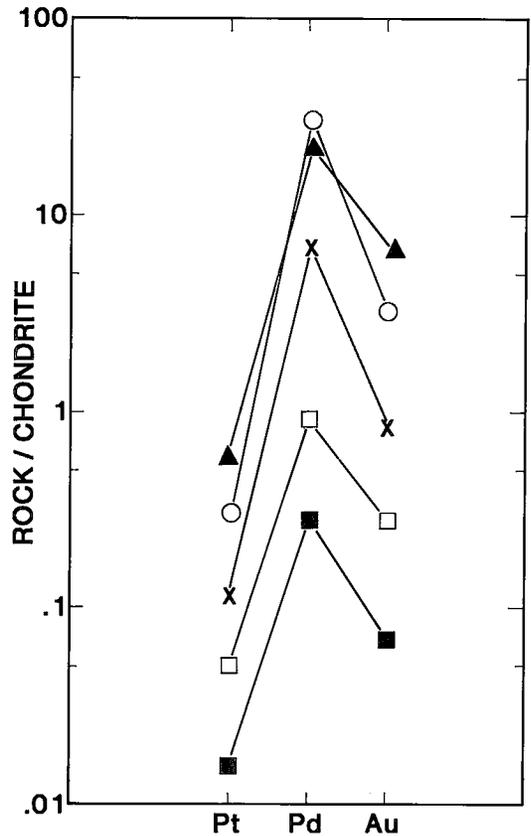


FIG. 5. Composite chondrite-normalized plot of whole-rock PGE values for all LDI rocks except amphibolite. Symbols: ● amphibolite, ○ bronzite gabbro, × norite, ▲ augite norite, ■ felsic gabbro, □ anorthosite - felsic gabbro.

CONCLUSIONS

Although the occurrence of PGE in many layered mafic-ultramafic intrusive complexes may result from primary magmatic processes, deuteric alteration by magmatic fluids during late-stage crystallization (and metamorphism) probably redistributes and concentrates the PGE, notably Pd and Au. The operation of processes of hydrothermal or secondary concentration in other complexes is supported by geological, petrographic and mineralogical data. These features are: 1) the localization of PGE along and within faults and shear zones (Patterson & Watkinson 1984); 2) occurrence of the PGM and sulfides as fracture, grain-boundary and cleavage fillings, angular polycrystalline aggregates, and mineral replacements; 3) the association of the PGE with secondary sulfides and selenides (*e.g.*, violarite-siegenite, millerite, sphalerite, galena, clausenthalite,

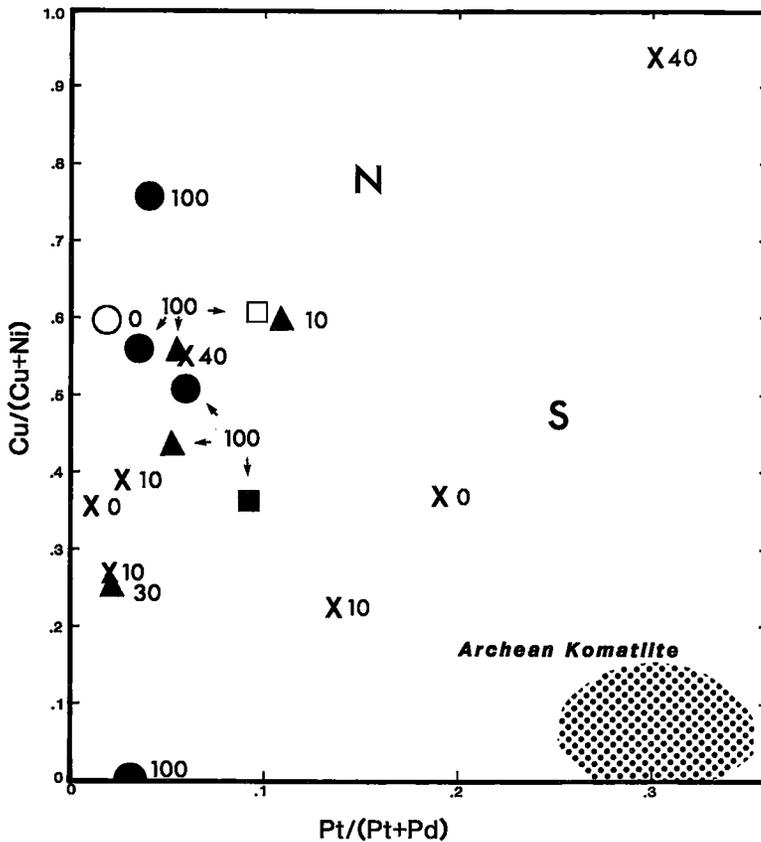


FIG. 8. Plot of $\text{Cu}/(\text{Cu} + \text{Ni})$ versus $\text{Pt}/(\text{Pt} + \text{Pd})$ ratios for all LDI lithologies. Symbols: N Noril'sk deposit, S Stillwater Complex. Archean komatiite field from Naldrett *et al.* (1980). All other symbols as in Figure 5.

etc.). There are, however, reported examples of hydrothermal ore deposits of PGE in metagabbroic rocks, *e.g.*, the New Rambler mine in Wyoming (McCallum *et al.* 1976).

At LDI, late-stage deuteric alteration or, less likely, greenschist-facies metamorphism caused by the emplacement of the Kenoran granites, remobilized and concentrated the PGE, Cu, Ni and S. The mobilization caused localized enrichment of PGE in the most severely affected lithologies, resulting in a lack of correlation between the PGE and Cu, Ni and S. This process has destroyed most primary magmatic PGM-sulfide-silicate assemblages and textures but has preserved the PGE abundance relationship $\text{Pd} > \text{Au} > \text{Pt}$, as confirmed by this study. Closely spaced sampling and finer petrographic control have necessitated this reinterpretation of the ap-

parently homogenized effect of using only 3-metre sections of drill core in interpreting the distribution of PGE from Lac-des-Iles.

ACKNOWLEDGEMENTS

This study was supported through a Research Agreement with RioCanex Inc.. We are extremely grateful to P. M. Kavanagh, T. J. Bottrill and C. H. Bertoni for their support and permission to publish this paper. Support was also provided through NSERC grant A7874. J. P. Sheridan kindly provided permission to study the Lac-des-Iles rocks and made data available to us. Discussions with Z. Johan and G. Dunning and typing by E. Lambton are gratefully acknowledged.

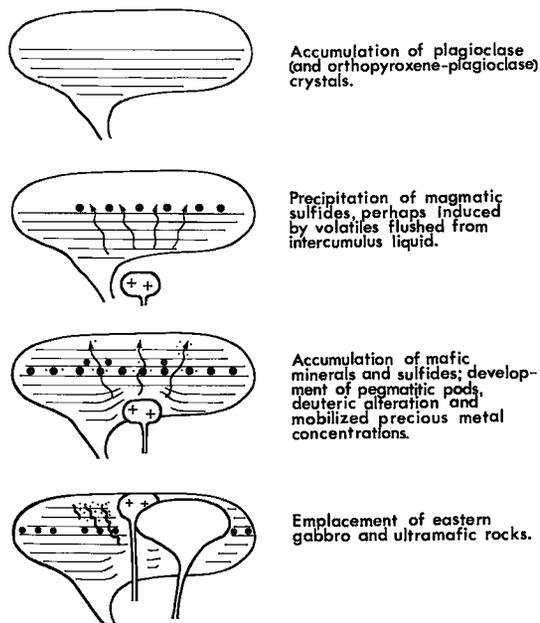


FIG. 9. Crystallization history and model of PGE concentration for the Lac-des-Iles Complex. Horizontal lines: layering, full circles: sulfides, crosses: eastern gabbro, blank: ultramafic intrusion, wavy lines: fractures.

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Received October 19, 1982, revised manuscript accepted July 30, 1983.