

## MINERAL VARIATION IN PROTEROZOIC DIABASE SILLS AND DYKES AT LAKE NIPIGON, ONTARIO

RICHARD H. SUTCLIFFE\*

Department of Geology, University of Western Ontario, London, Ontario N6A 5B7

### ABSTRACT

Middle Proterozoic olivine tholeiite diabase sills and dykes of the Lake Nipigon area, Ontario, were emplaced into Archean basement and Proterozoic metasediments. The diabase sills are 150 to 200 m thick and were intruded near the Archean-Proterozoic unconformity under a probable lithostatic load of less than 0.4 kbars. The major silicate phases in the sills and dykes are plagioclase (An<sub>75-7</sub>), variable proportions of augite (X<sub>Mg</sub> 0.79-0.30, Wo<sub>46-28</sub>) and pigeonite (X<sub>Mg</sub> 0.77-0.52, Wo<sub>18-8</sub>), olivine (Fo<sub>72-9</sub>), and minor orthopyroxene and a micrographic quartz - alkali feldspar intergrowth. Augite compositions are widely scattered between Wo<sub>28</sub> and Wo<sub>46</sub>. Variation of X<sub>Mg</sub> at constant Wo is attributed to stable equilibrium during fractional crystallization, whereas variations in Wo are probably due to metastable crystallization. Olivine grains are homogeneous and vary systematically with stratigraphic height. Mg-rich olivine (Fo<sub>72</sub>) in chilled diabase probably crystallized in equilibrium with basaltic liquid. Olivine in medium-grained diabase (Fo<sub>56-32</sub>) reacted with residual liquids. Fayalite (Fo<sub>9</sub>) occurs in pegmatitic diabase with a micrographic quartz-albite intergrowth. Plagioclase is the liquid phase in all of the diabases. Three variants of crystallization sequence, however, are defined by the order of crystallization of mafic minerals. These are: 1) olivine, augite, late pigeonite, 2) olivine, augite + pigeonite and 3) olivine, pigeonite, augite. Olivine persists throughout the sill section only in the sequence with late pigeonite. These variations are interpreted to reflect increasing activity of silica and may relate to the degree of contamination with siliceous crust. Fractionation in the sills is attributed to flowage differentiation and movement of residual liquids enriched in H<sub>2</sub>O, Na, and Fe toward the top of the sections.

**Keywords:** diabase, pyroxene, olivine, plagioclase, fractionation, Lake Nipigon, Ontario.

### SOMMAIRE

Des sills et des dykes de diabase tholéiitique à olivine, d'âge protérozoïque moyen, ont été mis en place dans le socle archéen et les sédiments protérozoïques de la région du lac Nipigon, en Ontario. Les sills, de 150 à 200 m en épaisseur, sont situés près de la non-conformité entre l'Archéen et le Protérozoïque, mis en place sous une pression lithostatique probable de moins de 0.4 kbars. Les phases silicatées les plus importantes sont: plagioclase

(An<sub>75-7</sub>), augite (X<sub>Mg</sub> 0.79-0.30, Wo<sub>46-28</sub>) en proportions variables, pigeonite (X<sub>Mg</sub> 0.77-0.52, Wo<sub>18-8</sub>), olivine (Fo<sub>72-9</sub>), et de faibles quantités d'orthopyroxène et d'une intercroissance micrographique de quartz et de feldspath alcalin. Les compositions d'augite varient fortement entre Wo<sub>28</sub> et Wo<sub>46</sub>. La variabilité en X<sub>Mg</sub> à teneur constante de Wo résulterait de l'équilibre au cours de la cristallisation fractionnée, tandis que les variations en Wo seraient probablement dues à une cristallisation métastable. Les cristaux d'olivine sont homogènes; leur composition varie de façon systématique avec le niveau stratigraphique. Une olivine magnésienne (Fo<sub>72</sub>) dans la bordure figée aurait cristallisé à l'équilibre dans le magma basaltique. L'olivine des diabases à granulométrie moyenne (Fo<sub>56-32</sub>) a réagi avec le liquide résiduel. La fayalite (Fo<sub>9</sub>) caractérise les facies pegmatitiques, qui contiennent une intercroissance micrographique de quartz + albite. Le plagioclase a cristallisé sur le liquidus dans tous les cas. Trois variantes de l'ordre de cristallisation dépendent des relations parmi les minéraux ferromagnésiens: 1) olivine, augite, pigeonite tardive, 2) olivine, augite + pigeonite, et 3) olivine, pigeonite, augite. L'olivine demeure présente dans le sill au complet seulement dans la paragenèse 1, où la pigeonite est tardive. Ces variations marqueraient l'augmentation progressive de l'activité de la silice, ce qui résulte peut-être du degré de contamination avec la croûte siliceuse. La fractionation dans les sills serait due à la différenciation par écoulement et au transfert des liquides résiduels enrichis en H<sub>2</sub>O, Na et Fe vers la partie supérieure des sections.

(Traduit par la Rédaction)

**Mots-clés:** diabase, pyroxène, olivine, plagioclase, fractionation, sills, lac Nipigon, Ontario.

### INTRODUCTION

Continental tholeiitic diabase sills and dykes provide an opportunity to examine the mechanisms of emplacement and crystallization of basaltic magma under geological conditions that can be well constrained. Recent studies have shown that although diabases commonly are superficially homogeneous, their mineralogical, compositional, and textural variations may provide sensitive indications of processes of magmatic evolution, emplacement and crystallization (e.g., Kretz *et al.* 1985, Hall *et al.* 1985).

In the Middle Proterozoic tholeiitic diabase of the Lake Nipigon area, different sections of the sills and dykes exhibit distinct trends of pyroxene variation and different sequences of crystallization of the mafic silicates. These differences form the basis of the

\*Present address: Ontario Geological Survey, 917-77 Grenville Street, Toronto, Ontario M7A 1W4.

present study. The petrology of diabase and associated picritic intrusive rocks of the Nipigon area, in relation to the evolution of the Keweenaw rift, has been documented by Sutcliffe (1987).

#### FORM OF THE SILLS

Mafic rocks in the Nipigon area consist of an early, volumetrically minor suite of picritic intrusive bodies and a later suite of olivine tholeiite diabase

sills, dykes and sheets (Sutcliffe 1987). The diabase sills were intruded into the Sibley Group, an undeformed sequence of Middle Precambrian epicontinental clastic metasediments (Franklin *et al.* 1980), and into Archean basement (Fig. 1). Zircon dating of the diabase sills (Davis & Sutcliffe 1985) indicates that they were emplaced,  $1108.8 \pm 4$  Ma ago and are contemporaneous with basaltic magmatism associated with Keweenaw rifting. These sills, informally referred to as the Logan sills (Stockwell *et al.* 1972),

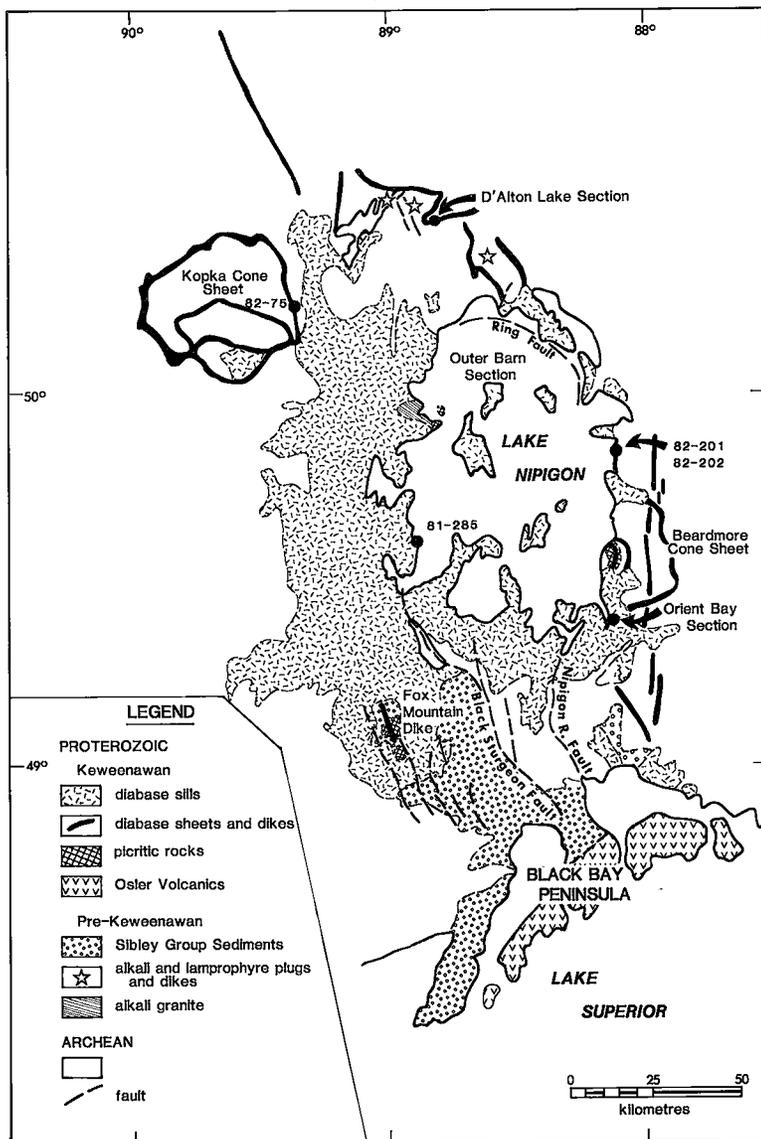


FIG. 1. Generalized geology of the Lake Nipigon area. Location of the sections sampled and of miscellaneous samples is shown. Geology from maps of the Ontario Geological Survey.

have a reversed magnetic polarity characteristic of the Lower Keweenaw (DuBois 1962). In this paper, "Nipigon sills" is used because the diabase sills in the study area do not have the characteristic high K, P, and Ti abundances and quartz-normative character of the type Logan sills (Weiblen *et al.* 1972).

One major diabase sill, 150 to 200 m thick, is exposed over most of the Nipigon area and locally is overlain by erosional remnants of an upper sill of comparable thickness. A few minor sills, 1 to 2 m thick, were observed at several locations, but no sills of intermediate thicknesses are known. Major sills have a textural stratigraphy consisting of: a lower chilled and aphanitic zone (2 to 3 m), an ophitic zone (30 to 60 m), a medium-grained zone (40 to 70 m), a pegmatitic zone (20 to 40 m), and an upper chilled and aphanitic zone (2 to 3 m) (Sutcliffe 1987). This stratigraphy illustrates that in most cases the diabase sills represent single cooling units.

The sills are near the unconformity between the Archean basement and overlying Middle Proterozoic Sibley metasediments. Chilled surfaces of the diabase sills show that host-rock inclusions are rare, and there is little evidence of assimilation of either Sibley metasediments or Archean basement by the diabase sills at the present level of erosion.

The overburden into which the sills were emplaced can be estimated using the 250-m average thickness of the Sibley Group (Franklin *et al.* 1980). Using an

average density of 2.5 g/cm<sup>3</sup> for the metasediments, overburden pressure at the time of sill emplacement was probably a minimum of 0.06 kbars. Higher estimates of the thickness of the Sibley Group, based on drilling and stratigraphic cross-sections, suggest pressures up to 0.4 kbars. These estimates assume that the sills predate Keweenaw volcanism, an interpretation that is supported by geochronological results (Davis & Sutcliffe 1985).

VARIATION OF MAJOR SILICATE PHASES

Samples from two diabase sections and additional rocks from diabase dykes and pegmatitic diabase were selected for microprobe analysis. Sample locations are given in Figure 1, and sample intervals are given with brief descriptions in Table 1. The Orient Bay section is a complete section of a typical diabase sill emplaced in the metasediments of the Rossport Formation in the southern part of Lake Nipigon. The D'Alton Lake section samples an inclined sheet emplaced in the Archean basement north of Lake Nipigon.

The typical diabase consists of euhedral, tabular plagioclase (An<sub>75-44</sub>), anhedral, interstitial to oikocrystic augite (X<sub>Mg</sub> 0.79-0.50, Wo<sub>40-30</sub>) [X<sub>Mg</sub> = Mg/(Mg + Fe<sup>2+</sup>)] and pigeonite (X<sub>Mg</sub> 0.65-0.52, Wo<sub>14-8</sub>), roundish to subhedral olivine (Fo<sub>70-32</sub>), and interstitial, anhedral magnetite and

TABLE 1. MAJOR ELEMENT CHEMISTRY OF THE DIABASE

	D'Alton Lake Section						Orient Bay Section							Others			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
SiO <sub>2</sub>	49.60	50.19	49.60	50.33	49.90	48.74	49.40	50.12	49.40	49.27	49.90	50.63	51.99	50.24	51.09	50.29	51.03
TiO <sub>2</sub>	1.53	1.57	1.48	1.61	0.93	1.82	1.03	1.30	.98	.89	0.93	1.11	1.07	1.73	1.95	2.99	1.47
Al <sub>2</sub> O <sub>3</sub>	15.85	13.91	15.04	13.79	15.58	15.77	15.04	14.90	15.99	15.61	15.58	13.64	13.40	14.30	14.11	10.56	14.67
FeO <sup>t</sup>	12.33	13.45	14.00	14.64	11.09	14.56	12.62	12.40	11.73	11.59	11.09	11.55	12.70	14.43	14.37	19.28	13.57
MnO	0.15	.21	.22	.23	.17	.22	.19	.19	.17	.18	.17	0.19	.23	.21	.21	.25	.20
MgO	5.74	6.22	6.53	6.08	7.67	6.08	8.73	7.66	8.30	8.78	7.67	7.04	7.25	6.33	5.54	4.13	6.02
CaO	11.04	11.23	10.16	10.60	11.91	9.94	10.47	10.51	10.49	10.95	11.91	12.13	10.76	9.90	9.77	8.65	9.98
Na <sub>2</sub> O	3.37	2.69	2.41	2.16	2.31	2.30	2.08	2.39	2.38	2.14	2.31	2.28	2.19	2.00	1.98	2.81	2.29
K <sub>2</sub> O	.22	.38	.41	.40	.37	.41	.36	.43	.48	.53	.37	0.32	.34	.80	.93	.83	.70
P <sub>2</sub> O <sub>5</sub>	.14	.14	.15	.15	.07	.15	.08	.09	.07	.06	.07	0.09	.06	.06	.06	.21	.06

D'Alton Lake Section

- 1 80-1116 Diabase chill.
- 2 80-1120 Fine-grained diabase, 0.5 m above base.
- 3 80-1117 Medium grained diabase, 4 m above base.
- 4 80-1121 Sub-chilled diabase from internal contact, 35 m.
- 5 80-1123 Medium grained diabase, 85 m.
- 6 80-1119 Medium grained diabase with pegmatitic patches, 140 m.

Orient Bay Section

- 7 81-267 Medium grained diabase, 5 m above base.
- 8 81-292 Medium grained, ophitic diabase, 15 m above base.
- 9 81-234 Medium grained, ophitic diabase.
- 10 81-290 Medium grained diabase, 77 m.
- 11 81-288 Medium grained diabase, 109 m.
- 12 81-286 Medium grained diabase, 125 m.
- 13 81-293 Medium grained diabase with pegmatitic patches, 140 m.

Others

- 14 82-201 Fe-rich diabase dike, Vint Bay, Lake Nipigon.
- 15 82-202 Medium grained diabase dike, Vint Bay.
- 16 81-285 Pegmatitic diabase from top of sill, Spruce Point, Lake Nipigon.
- 17 82-75 Medium grained diabase, Kopka River Cone sheet, Kenakskaniss Lake.

Recalculated to 100% anhydrous, Total iron as FeO<sup>t</sup>.

ilmeneite. Minor late orthopyroxene forms a rim on clinopyroxene. Accessory constituents are biotite, hornblende, "iddingsite", chalcopyrite and apatite. Variations in texture and grain size within sill sections are summarized by Sutcliffe (1987, Fig. 3).

Fine-grained, chilled diabase has an intersertal to intergranular texture, with 5 to 10% microphenocrysts. The microphenocryst assemblages in most examples of chilled diabase consist of plagioclase, plagioclase-olivine, and plagioclase-olivine-augite, and indicate a crystallization sequence of plagioclase, olivine, augite. Less commonly, the chilled diabase contains pigeonite and augite phenocrysts in addition to plagioclase and olivine.

### Analytical methods

The major-element composition of silicate minerals was determined with a Materials Analysis Company (MAC) 400 electron microprobe fitted with three automated spectrometers using a Krisel

Control automation system. Analyses were performed with an accelerating potential of 15 kV and a probe current of 250 or 500  $\mu$ A. MAGIC correction procedures were used.

The detection limit is approximately 0.05 wt.% oxide. Standard deviations of the  $2\sigma$  level on 9 determinations of a kaersutite standard are:  $\text{SiO}_2 \pm 0.84$ ,  $\text{TiO}_2 \pm 0.11$ ,  $\text{Al}_2\text{O}_3 \pm 0.22$ ,  $\text{Cr}_2\text{O}_3 \pm 0.02$ ,  $\text{FeO} \pm 0.27$ ,  $\text{MnO} \pm 0.03$ ,  $\text{MgO} \pm 0.26$ ,  $\text{CaO} \pm 0.22$ ,  $\text{Na}_2\text{O} \pm 0.12$ ,  $\text{K}_2\text{O} \pm 0.15\%$ .

Whole-rock major-element analyses were performed by X-ray fluorescence at the Geoscience Laboratories, Ontario Geological Survey, Toronto. Precision was reported by Sutcliffe (1987).

### Pyroxenes

Pyroxenes analyzed from the Orient Bay and D'Alton Lake sections and from diabase dykes and pegmatitic diabase (Table 2) show a wide range in composition (Fig. 2). Augite typically occurs as

TABLE 2. REPRESENTATIVE COMPOSITIONS OF PYROXENE

	Augite									Ca-poor Pyroxenes		
	1	2	3	4	5	6	7	8	9	10	11	12
SiO <sub>2</sub>	51.72	49.09	51.78	50.03	50.22	51.27	52.56	51.90	50.05	52.22	52.22	52.58
TiO <sub>2</sub>	.54	1.12	.51	.71	.65	.51	.31	.63	.62	.34	.39	.34
Al <sub>2</sub> O <sub>3</sub>	2.64	4.36	2.15	2.14	1.25	3.06	1.63	2.02	1.19	.87	.95	2.70
Cr <sub>2</sub> O <sub>3</sub>	.46	.18	.24	.28	.10	.27	.13	.00	.02	.15	.04	.19
FeO <sup>t</sup>	9.79	12.96	10.52	16.13	20.30	8.75	9.94	13.37	20.18	22.34	20.33	13.65
MnO	.22	.33	.28	.34	.48	.02	.06	.21	.45	.45	.40	.18
MgO	16.07	14.18	15.78	12.96	11.30	16.11	18.37	15.45	11.01	19.36	20.32	21.13
CaO	18.35	17.01	18.13	16.33	15.26	19.42	16.58	17.26	15.81	5.07	4.48	9.05
Na <sub>2</sub> O	.49	.56	.13	.10	.08	.00	.00	.00	.44	.00	.00	.09
Sum	100.28	99.79	99.52	99.02	99.64	99.41	99.58	100.84	99.77	100.81	99.13	99.91
Formulae based on 4 cations												
Si	1.906	1.839	1.934	1.923	1.950	1.905	1.941	1.929	1.939	1.956	1.968	1.928
Al	.115	.193	.095	.097	.057	.134	.071	.089	.054	.038	.042	.117
Fe <sup>2+</sup>	.237	.304	.317	.502	.652	.253	.281	.397	.603	.685	.641	.409
Fe <sup>3+</sup>	.065	.102	.012	.016	.007	.019	.026	.019	.051	.015	.000	.010
Mg	.883	.792	.878	.742	.654	.892	1.011	.856	.636	1.081	1.141	1.155
Mn	.007	.010	.009	.011	.016	.001	.002	.007	.015	.014	.013	.006
Ti	.015	.032	.014	.021	.019	.014	.009	.018	.018	.010	.011	.009
Cr	.013	.005	.007	.009	.003	.008	.004	.000	.001	.004	.001	.006
Ca	.725	.683	.725	.672	.635	.773	.656	.687	.656	.203	.181	.356
Na	.035	.041	.009	.007	.006	.000	.000	.000	.033	.000	.000	.006
Wo	39.29	38.39	37.78	35.07	32.71	40.30	33.68	35.43	34.63	10.33	9.22	18.53
X <sub>Mg</sub>	.79	.72	.74	.60	.50	.78	.78	.68	.51	.61	.64	.74

- 80-1116 (73) Diabase chill, D'Alton Lake, augite phenocryst core.
- 80-1116 (75) Diabase chill, D'Alton Lake, augite in matrix.
- 80-1123 (161) Medium grained diabase, D'Alton Lake, intersertal augite, sector core.
- 80-1123 (169) Medium grained diabase, D'Alton Lake, intersertal augite, sector rim.
- 80-1123 (166) Medium grained diabase, D'Alton Lake, intersertal augite, extreme sector.
- 81-292 (40) Medium grained diabase, Orient Bay, ophitic augite, core.
- 81-292 (41) Medium grained diabase, Orient Bay, ophitic augite.
- 81-292 (43) Medium grained diabase, Orient Bay, ophitic augite, rim.
- 81-285 (78) Pegmatitic diabase, Spruce Point, augite rim.
- 80-1123 (163) Medium grained diabase, D'Alton Lake, pigeonite rim on intersertal augite.
- 81-234 (108) Medium grained diabase, Orient Bay, ophitic pigeonite.
- 82-201 (120) Fe-rich diabase dike, chill, pigeonite overgrowth on olivine.

Total iron as FeO. numbers in parenthesis after sample number refer to analysis number.

X<sub>Mg</sub> = Mg/(Mg + Fe<sup>2+</sup>)

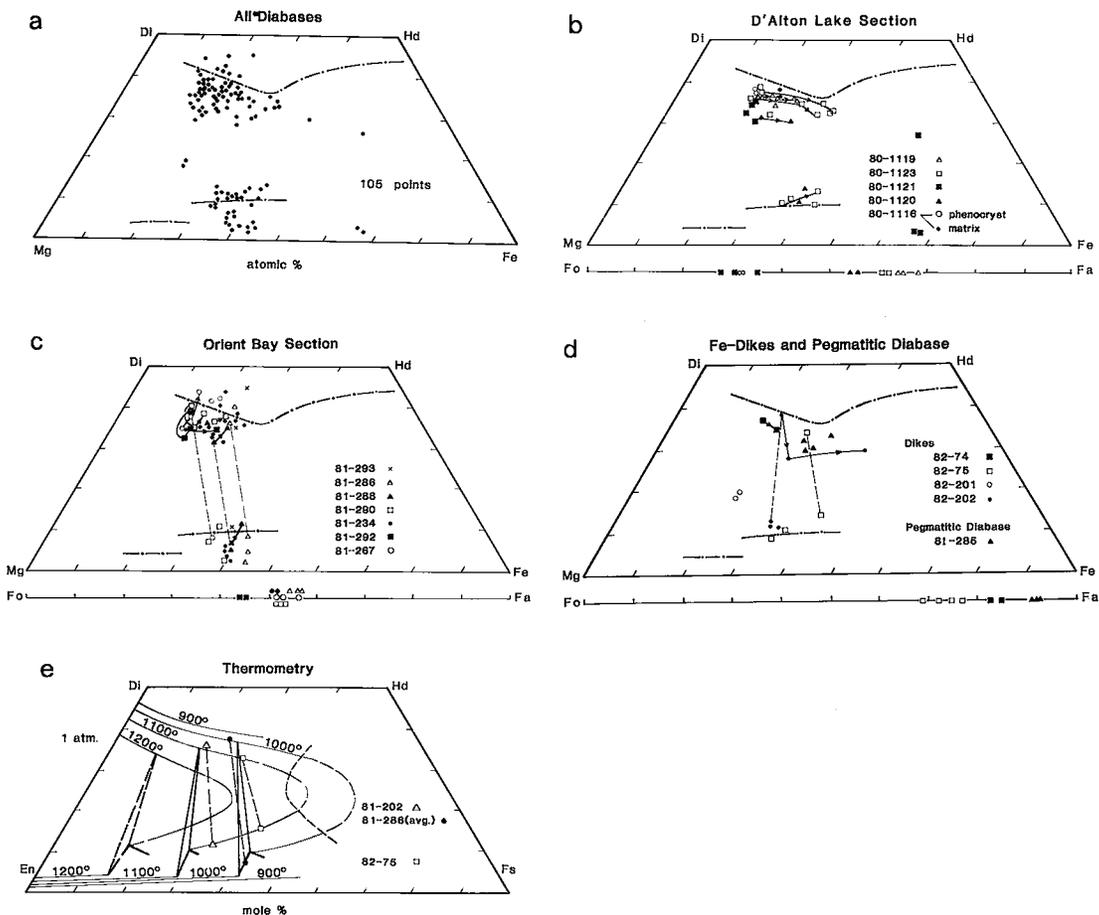


FIG. 2. Pyroxene and olivine chemistry (atomic %) in the Nipigon diabase. Dash-dot line represents the Skaergaard pyroxene trend. Solid lines with arrows indicate core-to-rim zoning. Dashed lines indicate Ca-rich and Ca-poor phases in contact. Sample numbers in b) and c) are arranged in stratigraphic order, with 80-1119 and 81-293 representing samples from the top of the respective sections. Isotherms in e) from Lindsley (1983).

coarse, well-developed subophitic to ophitic grains, composed of complex chemically zoned subgrains in which the crystallographic axes of individual crystals are nearly parallel. These textures are similar to those reported in other diabase suites, such as the Grenville swarm (Kretz *et al.* 1985). Ca-poor pyroxene is found as late-formed interstitial grains, subophitic grains that coprecipitated with augite, and early-formed phenocrysts. Augite from lower parts of the sills contains prominent blebby exsolution of Ca-poor pyroxene. In the center of sills, exsolution lamellae, where observed, are fine and not well developed. Late-formed Ca-poor pyroxene commonly contains blebby exsolution lamellae of augite.

The Nipigon augite compositions are Ca-poor in comparison to the Skaergaard trend (Fig. 2) but occupy a similar range to clinopyroxene from

Hawaiian tholeiites (Fodor *et al.* 1975). In most samples, Al varies between 1.5 and 2.5 wt.%  $Al_2O_3$ , and decreases with decreasing  $X_{Mg}$ .

The complex relationships of zoned subgrains make determination of coexisting phases difficult. Furthermore, as in many rocks in which the Ca-poor phase formed late, the determination of coexisting phases is of limited significance. Pairs of augite and pigeonite, which are interpreted to represent coexisting phases, are plotted on Lindsley's (1983) version of the pyroxene quadrilateral contoured for temperature (Fig. 2). The analyses refer to the core of coexisting subophitic grains (sample 81-286), and to coexisting pigeonite and augite phenocrysts in chilled diabase (samples 82-75 and 82-202). These pairs suggest that pyroxene crystallized over the approximate  $T$  range 1100–1000°C.

In the D'Alton Lake section (Fig. 2b), the most primitive augite ( $X_{Mg}$  0.79) is from a phenocryst in a chill zone. This composition is closely approached by the core of some subophitic grains. Ca-poor pyroxene in this section formed late and occurs at

the edge of augite grains as a sector or a rim. Pyroxenes from the D'Alton Lake section show no significant compositional variation with stratigraphic height.

Marked variation in complex single subophitic grains parallels the Mg-rich augite trend of the Skaergaard Complex (Deer *et al.* 1978). The variation in  $X_{Mg}$  within single mm-sized grains is of the same magnitude as the variation over the entire sill section. These subophitic grains (Fig. 3a) consist of several sectors in optical near-continuity. At least one sector in Figure 3a shows Fe enrichment toward the sector edge. Sectors near the edge of composite grains show a further Fe enrichment relative to sectors near the center of the grain.

In the Orient Bay section (Fig. 2c), both augite and pigeonite occur as subophitic grains that texturally appear to have crystallized together. The augite and pigeonite commonly form composite grains in which the crystallographic axes are nearly parallel (Fig. 3c). These composite grains show complex chemical zoning, but with somewhat less Fe enrichment in the augite compared to the D'Alton Lake section. Instead, the augite has variable Ca contents. Several grains show an initial trend to lower Ca, resembling the quench trend of Smith & Lindsley (1971), but subsequently trend to higher Ca. Individual samples from the Orient Bay section show a slight decrease in  $X_{Mg}$  with increasing stratigraphic height, although there is considerable overlap due to within-sample variation.

Tie lines between coexisting pyroxenes in the Orient Bay section show that the Ca-poor pyroxene phase is Fe-rich relative to experimentally determined tie lines (Lindsley 1983) and tie lines from pyroxenes of other typical tholeiitic suites (Deer *et al.* 1978). The slopes of the tie lines are comparable to those determined by Konda (1970) for the Keweenaw Beaver Bay Complex in Minnesota, in which the Fe-rich nature of pigeonite is attributed to late crystallization. Fe-rich orthopyroxene ( $X_{Mg}$  0.29,  $Wo_3$ ) occurs as a late phase in some samples.

The pyroxenes of the diabase dykes display complex compositional variation (Fig. 2d). In diabase chill-zone sample 82-201, pigeonite with a composition in the metastable field occurs as a phenocryst phase. The pigeonite is clustered around small corroded olivine phenocrysts (Fig. 3d), suggesting that olivine and melt have reacted to form pigeonite. In most other diabases from Nipigon, olivine appears to be in equilibrium with phenocrystic augite. Sample 82-202, from a fine-grained diabase of the same dyke, contains sector-zoned augite with pigeonite in sectors and in the core. An irregular ragged core of pigeonite in these grains suggests that pigeonite and melt have reacted to form augite. Compositional variation in a zoned augite grain (sample 82-202) is shown in Figure 2d.

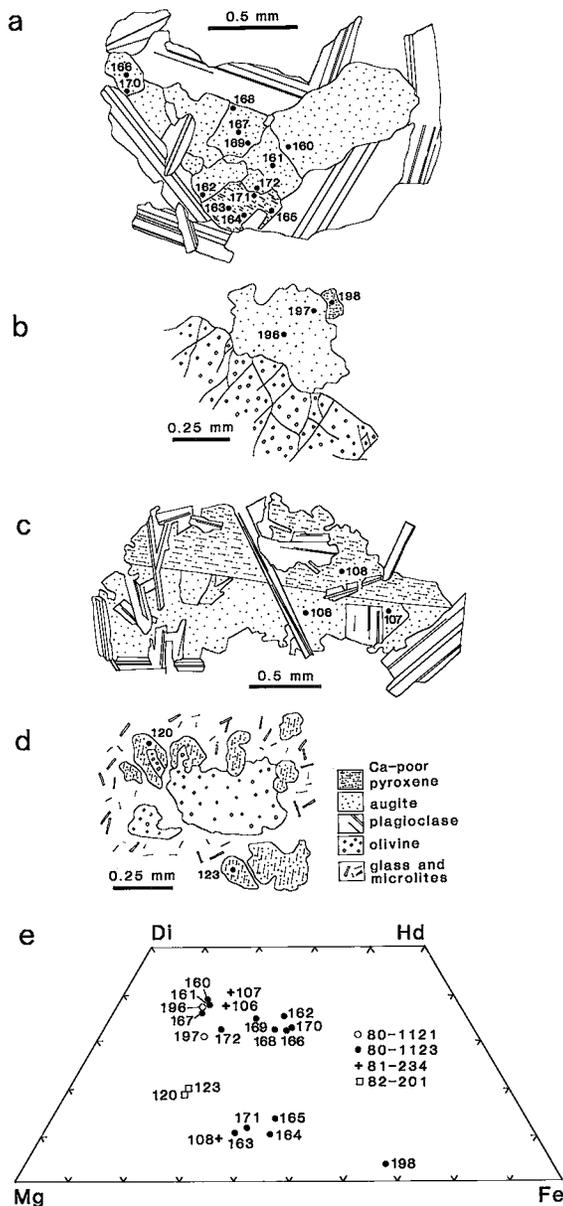


FIG. 3. Details of pyroxenes from selected samples. a) Augite with late pigeonite, sample 80-1123. b) Augite overgrowth on olivine with late orthopyroxene, sample 80-1121. c) Ophitic augite and pigeonite, sample 81-234. d) Pigeonite overgrowth on olivine, sample 82-201. Numbered points refer to compositions in e).

*Olivine*

Olivine is found in most of the diabbases sampled in the Lake Nipigon area, an exception being in the upper part of the Orient Bay section. A wide range in composition (Fo<sub>72-9</sub>) is observed (Table 3, Fig. 2). Olivine in medium-grained diabase ranges in composition from Fo<sub>56</sub> to Fo<sub>32</sub>. This olivine occurs as 0.1- to 1.5-mm round grains that are usually enclosed by oikocrystic augite. A few samples contain anhedral olivine interstitial to plagioclase.

Fayalite (Fo<sub>9</sub>) occurs as anhedral grains up to 2 mm in diameter in association with a quartz-albite granophyric intergrowth in pegmatitic diabase (sample 81-285). This is the most Fe-rich olivine observed in the suite. A medium-grained diabase with pegmatitic patches (sample 80-1119) from the D'Alton Lake section contains olivine of composition Fo<sub>32-36</sub>. This diabase contains a quartz - alkali feldspar granophyric intergrowth with which the olivine is not in contact.

The most magnesian olivine, Fo<sub>72-69</sub>, occurs as phenocrysts in chilled phases of the D'Alton Lake section. Olivine in medium-grained diabbases from the D'Alton Lake and Orient Bay sections show the ranges Fo<sub>46-32</sub> and Fo<sub>56-44</sub>, respectively. In both sections, Fo content decreases with increasing strati-

TABLE 3. REPRESENTATIVE COMPOSITIONS OF OLIVINE

	1	2	3	4	5	6	7	8	9
SiO <sub>2</sub>	38.29	34.98	34.19	33.73	36.30	35.02	34.01	34.15	30.73
Al <sub>2</sub> O <sub>3</sub>	.00	.03	.03	.00	.00	.00	.00	.02	.00
TiO <sub>2</sub>	.01	.04	.09	.00	.00	.02	.00	.13	.03
Cr <sub>2</sub> O <sub>3</sub>	.07	.17	.05	.00	.04	.00	.11	.02	.00
FeO	24.61	41.95	47.66	49.69	36.92	41.55	44.22	47.80	63.95
MgO	.32	.00	.02	.00	.15	.10	.16	.53	.02
MnO	36.39	21.85	17.70	15.38	25.68	22.39	19.96	16.32	3.72
CaO	.23	.66	.84	.64	.50	.58	.66	.82	.91
Total	100.11	99.88	100.72	99.84	99.81	99.76	99.28	100.17	99.74
Formulae on a basis of 4 oxygen									
Si	1.007	1.009	1.007	1.015	1.018	1.009	1.002	1.017	1.010
Al	.000	.001	.001	.000	.000	.000	.000	.001	.000
Ti	.000	.001	.002	.000	.000	.000	.000	.003	.001
Cr	.001	.004	.001	.000	.001	.000	.003	.000	.000
Fe	.541	1.012	1.174	1.251	.866	1.001	1.090	1.190	1.757
Mg	.007	.000	.000	.003	.003	.002	.004	.013	.001
Mn	1.426	.939	.777	.690	1.074	.961	.877	.724	.182
Ca	.005	.016	.021	.016	.012	.014	.016	.021	.025
Fo	.005	.006	.004	.009	.007	.003	.005	.012	.013
Fo	72.49	48.14	39.84	35.55	55.35	48.99	44.58	37.83	09.61

- 80-1161 (16) Olivine phenocryst core, diabase chill, D'Alton Lake.
- 80-1120 (24) Olivine core, medium grained diabase D'Alton Lake.
- 80-1123 (29) Olivine, medium grained diabase D'Alton Lake.
- 80-1119 (34) Olivine core, diabase with pegmatitic patches, D'Alton Lake.
- 81-292 (45) Olivine core, medium grained diabase, Orient Bay.
- 81-290 (41) Olivine core, medium grained diabase, Orient Bay.
- 81-288 (37) Olivine core, medium grained diabase, Orient Bay.
- 82-75 (10) Olivine core, medium grained Fe-diabase dike.
- 81-285 (30) Pegmatitic diabase, Spruce Point, olivine with quartz.

TABLE 4. REPRESENTATIVE COMPOSITIONS OF FELDSPAR

	1	2	3	4	5	6	7	8	9	10	11	12
SiO <sub>2</sub>	52.20	51.91	51.57	52.10	51.05	52.90	51.09	55.36	53.76	58.50	64.36	65.89
Al <sub>2</sub> O <sub>3</sub>	30.38	29.22	29.77	29.31	29.49	29.77	29.77	26.81	28.36	25.21	18.72	20.77
FeO	.80	.80	.48	.60	1.34	.54	.55	.71	.37	.32	.48	.21
Na <sub>2</sub> O	3.43	3.84	4.50	4.34	3.42	4.07	3.67	5.68	4.21	6.60	2.55	11.04
CaO	14.12	13.44	13.04	12.96	14.24	12.89	14.00	10.21	12.44	8.79	.23	1.48
K <sub>2</sub> O	.13	.11	.16	.23	.54	.25	.22	.23	.17	.43	12.66	.95
Total	101.06	99.12	98.52	99.54	100.08	100.42	99.30	99.00	99.31	99.85	99.00	100.34

Formulae on a basis of 32 oxygen

Si	9.420	9.538	9.451	9.540	9.373	9.574	9.397	10.105	9.803	10.521	11.903	11.612
AlIV	6.460	6.327	6.429	6.324	6.381	6.349	6.452	5.767	6.094	5.343	4.080	4.313
Fe	.121	.123	.074	.092	.206	.082	.085	.108	.056	.048	.074	.031
Ca	2.730	2.646	2.560	2.542	2.801	2.500	2.759	1.997	2.430	1.694	.046	.379
Na	1.200	1.297	1.599	1.541	1.217	1.428	1.309	2.010	1.488	2.301	.914	3.722
K	.030	.026	.037	.054	.126	.058	.052	.054	.040	.099	2.986	.214
Ab	30.30	32.88	38.10	37.24	29.37	35.83	31.77	49.51	37.60	56.22	23.17	88.44
An	68.94	66.67	61.01	61.46	67.58	62.72	66.98	49.18	61.40	41.37	1.15	6.55
Or	.76	.65	.89	1.30	3.05	1.45	1.25	1.32	1.00	2.41	75.68	5.01

- 80-1116 (83) Phenocryst core, diabase chill, D'Alton Lake.
- 80-1116 (85) Phenocryst rim, diabase chill, D'Alton Lake.
- 80-1120 (80) Plagioclase core, medium-grained diabase, D'Alton Lake.
- 80-1119 (117) Plagioclase core, medium-grained diabase with pegmatitic patches, D'Alton Lake.
- 81-292 (23) Plagioclase core, medium-grained diabase, Orient Bay.
- 81-290 (32) Plagioclase core, medium-grained diabase, Orient Bay.
- 81-288 (17) Plagioclase core, medium-grained diabase, Orient Bay.
- 81-288 (19) Plagioclase rim, medium-grained diabase, Orient Bay.
- 81-286 (15) Plagioclase core, medium-grained diabase, Orient Bay.
- 81-286 (16) Plagioclase rim, medium-grained diabase, Orient Bay.
- 80-1119 (115) K-spar in intergrowth, medium-grained diabase with pegmatitic patches, D'Alton Lake.
- 81-285 (95) Albite in intergrowth, pegmatitic diabase, Spruce Point.

graphic height. The more magnesian olivine of the Orient Bay section reflects a slightly more magnesian bulk-composition for this section. In all cases, the olivine has a low Cr content, from 0.21 wt.%  $\text{Cr}_2\text{O}_3$  in phenocrysts to less than 0.05 wt.% in the medium-grained diabase.

### Feldspar

Plagioclase from Nipigon diabases has a wide range in An content (Table 4, Fig. 4). In medium-grained diabase, the plagioclase occurs as euhedral, tabular to lath-shaped grains 1.5 to 4 mm long, with well-developed albite, Carlsbad and pericline twinning.

In the D'Alton Lake section (Fig. 4), the most calcic plagioclase ( $\text{An}_{71}$ ) occurs as phenocrysts in chilled diabase. The phenocrysts generally have normal core-to-rim variation, in the range  $\text{An}_{70-68}$ . Some oscillatory zoning occurs, with compositions ranging from  $\text{An}_{71}$  to  $\text{An}_{65}$ . Plagioclase in the matrix ranges from  $\text{An}_{56}$  to  $\text{An}_{45}$ .

Drake (1976) has evaluated the equilibrium constant for the distribution of the albite component between plagioclase and melt. This approach allows the temperature of crystallization of a given plagioclase composition formed from a dry melt of known composition at low  $P$  to be calculated. Maximum An contents of plagioclase phenocrysts in two chilled diabases in the D'Alton Lake section (80-1120 and 80-1121) yield temperatures of 1113 and 1045°C, respectively. This calculation assumes that the chilled diabases represent liquid compositions that have not been substantially modified by the accumulation of phenocrysts.

Tabular plagioclase from medium-grained diabase of the D'Alton Lake section ranges from  $\text{An}_{67}$  to  $\text{An}_{43}$ . Rims are generally more Na-rich, but weak oscillatory zoning is characteristic. There is a weak trend of Na enrichment toward the top of the sill. At the top of the sill, a granophyric intergrowth of alkali feldspar ( $\text{An}_1\text{Ab}_{26}\text{Or}_{73}$ ) and quartz coexists with sodic oligoclase ( $\text{An}_{23}\text{Ab}_{73}\text{Or}_4$ ).

The Orient Bay section (Fig. 4) shows a similar

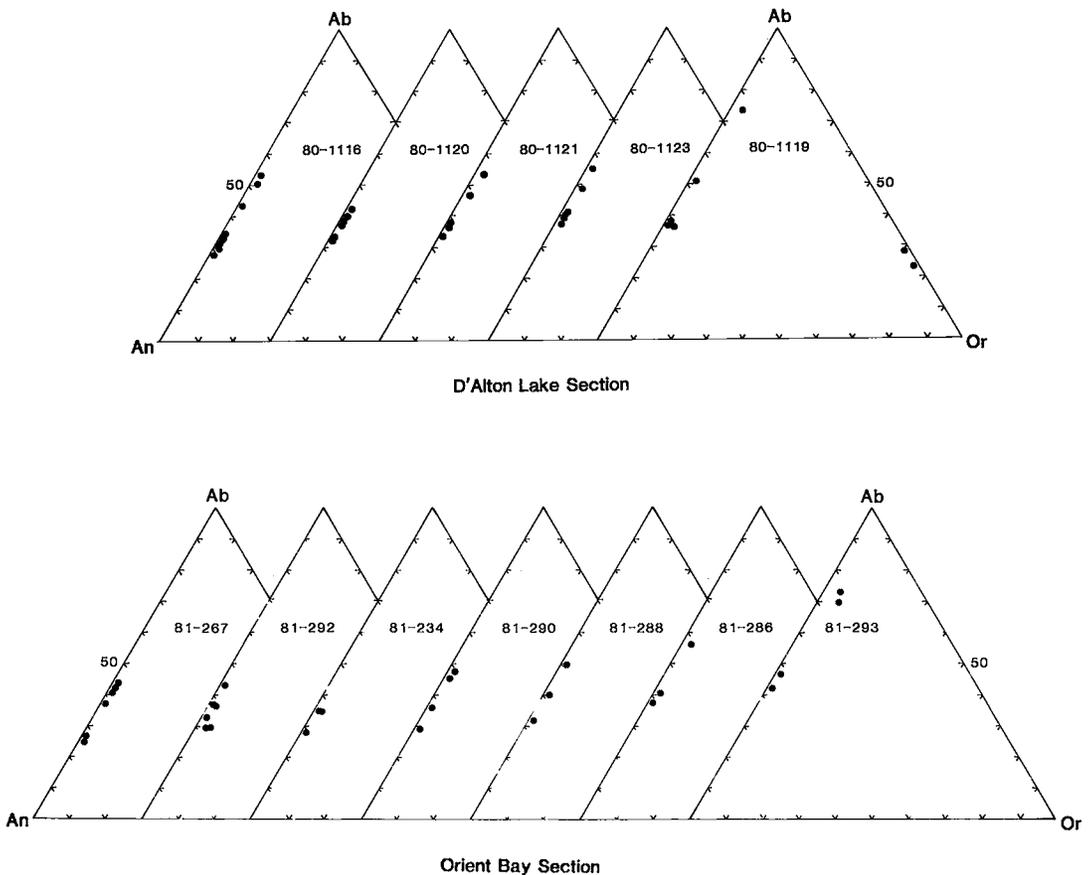


FIG. 4. Feldspar compositions in the Nipigon diabase. Samples are identified in Table 1 and are presented in order of increasing stratigraphic height from left to right.

range in plagioclase composition (An<sub>74-41</sub>), and also has a weak trend to Na enrichment with increasing stratigraphic height. All samples of the section, however, show normal zoning, with up to 20 mole % difference in core-to-rim variation. The most calcic composition is found in the core of plagioclase grains enclosed by augite oikocrysts. At the top of the section, oligoclase An<sub>22</sub>Ab<sub>73</sub>Or<sub>5</sub> is intergrown with quartz.

A pegmatitic diabase (81–285) exhibits tabular plagioclase with normal zoning: An<sub>45-31</sub>Ab<sub>53-66</sub>Or<sub>2-3</sub>. This sample contains a graphic intergrowth of albite (An<sub>7</sub>Ab<sub>88</sub>Or<sub>5</sub>) and quartz.

## DISCUSSION

### Cooling

Heat-flow calculations of Jaeger (1957) provide estimates of the time-span of crystallization. A crystallization interval of 200°C with a temperature of intrusion of 1100°C is assumed. This is based on an analogy with the Palisades sill (Walker *et al.* 1973, Shirley 1987). The range in temperature is consistent with calculations from pyroxene and feldspar in the Nipigon sills. Using assumptions of Jaeger (1957) (intrusion is instantaneous, initial temperature of wallrock is 0°C, latent heat of crystallization is 100 cal/g, the density of melt and country rock is 2.8 g/cm<sup>3</sup>, the specific heat of melt and country rock are 0.30 and 0.25 cal/g-deg, respectively, and thermal conductivity of melt and country rock is 0.0005), the time for crystallization is 0.012 *D*<sup>2</sup> years, where *D* is the thickness of the sill in meters. This calculation suggests that the Nipigon sills, which are 150 to 200 m thick, crystallized over approximately 210 to 480 years. Since major-element chemistry suggests injection of multiple pulses of magma (Sutcliffe 1987), the assumption of instantaneous intrusion is an oversimplification. However, the textural stratigraphy of most sills, with ophitic zones confined to the base, and pegmatitic diabase, to the top, indicates that the sills cooled as single units.

### Olivine compositions and silica activity

Olivine in the Nipigon sills ranges in composition from Fo<sub>72</sub> to Fo<sub>9</sub>. The most magnesian olivine compositions occur in phenocrysts in chilled phases of the D'Alton Lake sill; these are in equilibrium with liquids having MgO/(MgO + FeO) (molar) equal to 0.44, based on the equilibrium distribution-coefficient of 0.30 (Roeder & Emslie 1970) for the Mg-Fe exchange reaction. This value is close to the value of Mg' [MgO/(MgO + 0.9FeO<sup>0</sup>)] of the chill-zone samples.

Olivine from the medium-grained diabase is considerably less Mg-rich (Fo<sub>56-32</sub>). This olivine is inter-

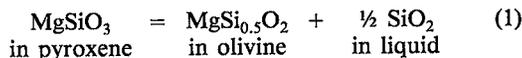
preted to have crystallized after liquidus plagioclase, but prior to augite. Based on the Mg-Fe exchange reaction, this olivine is in equilibrium with a liquid having a MgO/(MgO + FeO) value less than 0.275. The olivine should not have crystallized from a liquid with Mg' of 0.44 to 0.54 (corresponding to the Mg' of the diabase). The iron-rich nature of the olivine is therefore probably related to equilibrium with residual liquid. In comparison with coexisting Ca-poor pyroxene and olivine in the Skaergaard Complex, Nipigon diabases exhibit similar compositions for coexisting olivine and late Ca-poor pyroxene.

The stability of Ca-poor pyroxene relative to olivine is dependent on the silica activity of the magma (Morse 1980). In the presence of excess silica, the olivine reacts with liquid to form Ca-poor pyroxene. Olivine and pigeonite in the D'Alton Lake and Orient Bay sections display distinct sequences of crystallization that can be related to silica activity in the magma.

The D'Alton Lake sill contains olivine throughout the section, but Ca-poor pyroxene was not found in the uppermost part. The last sample in which pigeonite is recognized contains olivine of composition Fo<sub>40</sub>. This is the same olivine composition for which Ca-poor pyroxene disappears in the Skaergaard sequence (Wager & Brown 1968). In the Skaergaard Complex, pigeonite of En<sub>49</sub> coexists with olivine of Fo<sub>40</sub>. The corresponding D'Alton Lake pigeonite is En<sub>48</sub>.

In contrast, no olivine was found in the upper part of the Orient Bay section, but Ca-poor pyroxene persists throughout the sequence. This combination implies a higher *a*(SiO<sub>2</sub>) than in the D'Alton sequence. The observations agree with the finding that augite and pigeonite probably coprecipitated in the Orient Bay sequence, whereas in the D'Alton Lake section, pigeonite crystallized late in the sequence.

Compositions of coexisting pigeonite and olivine in both the D'Alton Lake and Orient Bay sections allow estimates of *a*(SiO<sub>2</sub>) to be calculated based on the reaction



For reaction (1), the equilibrium constant for a given temperature and pressure can be given as

$$K = \frac{a_{\text{MgSi}_{0.5}\text{O}_2} \cdot a_{\text{SiO}_2}^{0.5}}{a_{\text{MgSiO}_3}} \quad (2)$$

Values of *a*(MgSi<sub>0.5</sub>O<sub>2</sub>) and *a*(MgSiO<sub>3</sub>) can be estimated from the mole fractions of these components in olivine and pyroxene, respectively, using activity coefficients given by Williams (1971, 1972). The equilibrium constant for the end-member reaction

(2) has been evaluated for cases in which olivine and pyroxene have intermediate values of  $X_{Mg}$  (Morse 1979).

A  $T$  of 1000°C and a  $P$  of 400 bars are assumed for the late crystallization of pigeonite. The equilibrium constant is relatively insensitive to changes in  $P$  within the range of conditions for the Nipigon sills. Compositions of olivine and pigeonite in contact in the D'Alton Lake section are:  $Fo_{40}$  and  $X_{Mg} = 0.54$ ,  $Wo_{10}$ ;  $Fo_{47}$  and  $X_{Mg} = 0.57$ ,  $Wo_{12}$ . These compositions indicate silica activities of 0.83 and 0.71. Composition of olivine and pigeonite in contact in the Orient Bay section are:  $Fo_{45}$  and  $X_{Mg} = 0.59$ ,  $Wo_{7.2}$ ;  $Fo_{48}$  and  $X_{Mg} = 0.63$ ,  $Wo_{11.8}$ ;  $Fo_{50}$  and  $X_{Mg} = 0.60$ ,  $Wo_{6.9}$ . These compositions indicate silica activities of 0.81, 0.78 and 0.76, respectively. The estimates of silica activity are sensitive to the mineral compositions and therefore are dependent on the interpretation of which phases actually coexisted. The estimates, however, are in agreement with the interpretation of  $a(SiO_2)$  based on petrographic observations. The D'Alton Lake section has lower  $a(SiO_2)$  for comparable olivine compositions. The  $a(SiO_2)$  for coexisting pigeonite ( $En_{49}$ ) and olivine ( $Fo_{40}$ ) of the Skaergaard Complex is estimated at 0.9 by Morse (1980). The Nipigon diabases have slightly lower calculated  $a(SiO_2)$ , in agreement with the persistence of olivine throughout most of the sequence. Other Keweenaw tholeiites are also interpreted to have a low  $a(SiO_2)$  relative to typical tholeiite suites (Konda & Green 1974).

The presence of quartz in the late residuum of pegmatitic diabase indicates that  $a(SiO_2)$  rose to unity at the late stages of crystallization of the Nipigon diabases. The stable assemblage in these rocks is augite + fayalite + quartz.

#### *Pyroxene variation and crystallization sequences*

Pyroxenes in the Nipigon sills exhibit different sequences of crystallization and different compositional trends. Diabases from the D'Alton Lake section reveal the sequence of mafic-mineral crystallization olivine, augite, and late pigeonite. This sequence is typical of oceanic tholeiites fractionated at low pressure (Longhi 1981) and is the same as that determined by Konda & Green (1974) for Keweenaw basalts. In the Orient Bay section, augite and pigeonite coprecipitated over a wider range of crystallization, as indicated by the presence of subophitic grains of both phases. A small group of Fe-rich diabase is characterized by the crystallization of pigeonite phenocrysts as a result of the reaction of olivine and melt, prior to the crystallization of augite. The early crystallization of a Ca-poor pyroxene is characteristic of continental tholeiites, but is anomalous for oceanic mantle-derived magmas (Longhi 1981, Campbell 1985).

Arndt & Fleet (1979) reported that under conditions of strong undercooling in komatiitic flows, metastable pigeonite crystallizes at the expense of diopside. Undercooling may explain the early crystallization of pigeonite in the Fe-rich Nipigon diabases; however, a compositional control on the crystallization sequence is preferred because pigeonite is absent in chill zones of more magnesian diabases.

The difference between the crystallization sequences is summarized in Figure 5. A typical sequence of fractionation from an oceanic mantle-derived melt will follow the path ABCD, and augite will crystallize before pigeonite. This sequence is represented by the D'Alton Lake section. In an alternative sequence, for equilibrium crystallization, the liquid will follow the path EFCD, and Ca-poor pyroxene will crystallize first. This sequence may be represented by the Fe-rich diabase dykes. The Orient Bay section may represent an intermediate sequence of crystallization, in which the fractionating melt reaches the olivine-pyroxene cotectic near C. The differences in crystallization sequence may reflect differences in mantle-source compositions; however, Longhi (1981) and Campbell (1985) have suggested that the early crystallization of Ca-poor pyroxene may result from the assimilation of siliceous country-rock by the primary melt before significant fractionation, resulting in the path AEFCD.

Chemical variation in Nipigon pyroxenes occurs on a scale of 1–2 mm grains. Within-grain variation obscures systematic variation throughout the sill sections. The two trends of within-grain variation are exhibited by the Orient Bay and D'Alton Lake sections (Fig. 3). The trend of decreasing  $X_{Mg}$  at relatively constant  $Wo$  exhibited by the D'Alton Lake section is similar to the trend of intratelluric fractionation of Muir & Tilley (1964), and is similar but somewhat less calcic than that reported by Konda & Green (1974) in the Keweenaw lavas of Minnesota. The trend in the Orient Bay section involves decreasing  $X_{Mg}$  and variable  $Wo$ . This resembles the Ca-Fe substitution along the "quench trend" of Smith & Lindsley (1971).

Yamakawa (1971) described two contrasting trends of pyroxene crystallization from a single tholeiitic diabase sill in Japan: a trend of decreasing  $X_{Mg}$  at constant  $Wo$  is accounted for by cotectic crystallization of Ca-rich and Ca-poor pyroxene; a second trend of decreasing  $X_{Mg}$  and decreasing  $Wo$  is explained as metastable crystallization resulting from undercooling of the liquid with respect to pigeonite. In the case of the D'Alton Lake section, the former trend may reflect cotectic crystallization of augite and olivine, as the  $a(SiO_2)$  in the liquid was too low to allow Ca-poor pyroxene to crystallize until the final stages of solidification. For the Orient Bay section, in which two pyroxene phases coprecipitated over a wider interval of crystallization, the second expla-

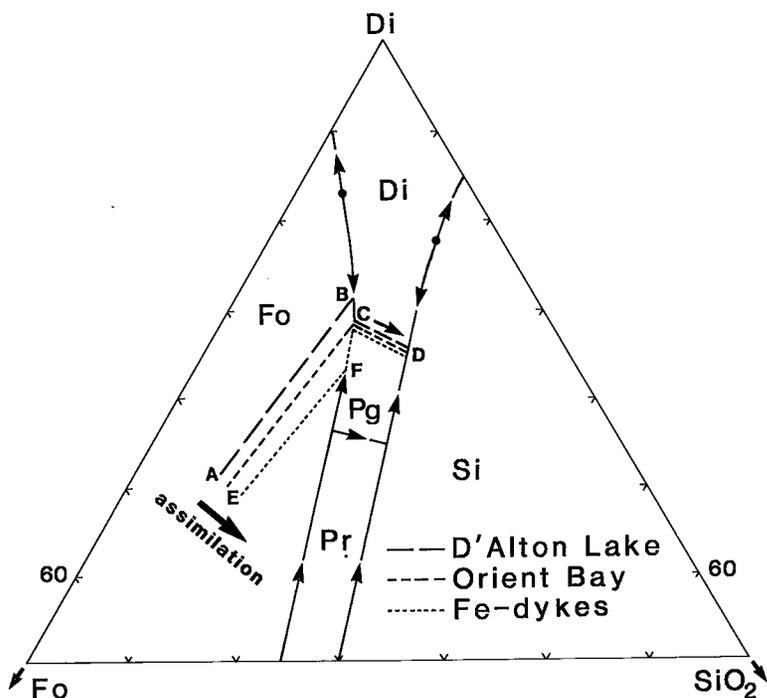


FIG. 5. Part of the equilibrium phase-diagram for the system forsterite-diopside-silica after Kushiro (1972) and Morse (1980). Mantle-derived magmas at point A fractionate along path ABCD, magmas mixed with siliceous crust move to point E and fractionate along path EFCD (Longhi 1981, Campbell 1985). Possible differentiation paths for rocks from Lake Nipigon are shown. Fo forsterite, Pr "protoenstatite", Pg pigeonite, Di diopside, Si silica.

nation seems to be appropriate. The variation in pyroxene chemistry on the scale of individual composite grains indicates that early-formed pyroxene failed to react with remaining melt, and that fractional crystallization took place on the scale of cells of interstitial liquid.

#### *Differentiation processes*

The presence of local accumulation of olivine in the lower parts of the D'Alton Lake section (Sutcliffe 1987) suggests that crystal fractionation may have resulted in the evolution of liquid composition within the sills. Other major sills in the Nipigon area, however, have accumulations of olivine near the center of the sills (Sutcliffe 1987). Crystal fractionation may have taken place by crystal settling (Walker 1970) or by flowage differentiation (Bhattacharji & Smith 1964). The effectiveness of crystal settling is determined by the settling velocity and convective velocity (Marsh & Maxey 1985). Calculations for the Palisades sill suggest that convective velocities are orders of magnitude higher than the settling veloci-

ties, and lead to the expectation that crystals would be uniformly distributed in the magma (Shirley 1987). An alternative explanation for fractionation in the Palisades sill given by Shirley (1987) is the mechanism investigated by Brandeis & Jaupart (1986) in which material crystallized on the roof falls to the sill floor as plumes that deposit crystal-rich suspensions. Given that multiple injections of magma occurred in the Nipigon sills, and that olivine is concentrated at different levels within the sills (Sutcliffe 1987), flowage differentiation may have been the dominant process of accumulation of olivine.

Systematic variation in the compositions of olivine and plagioclase with stratigraphic height, and an increase in proportion of the micrographic quartz-feldspar intergrowth toward the top of the sills, indicate that during the late stages of crystallization the magma became more evolved toward the top of the sills. This result may have been achieved through a combination of flowage differentiation to accumulate suspended minerals, and postcumulus transport of residual liquids enriched in  $H_2O$ , Na and Fe toward the top of the section. This reason-

ing is similar to that suggested by Jones (1984) as a process of differentiation in Keweenawan diabase sills in Cook County, Minnesota, and by Shirley (1987) for the Palisades sill.

#### CONCLUSIONS

1. The major sills are 150 to 200 m thick. The textural stratigraphy, which varies from a lower ophitic zone to an upper pegmatitic zone, indicates that in most cases the sills cooled as single units. The sills probably took 200 to 500 years to solidify.
2. The pyroxenes exhibit marked within-sample chemical variation. A trend of decreasing  $X_{Mg}$  at constant Wo reflects a fractionation trend. A second trend of decreasing  $X_{Mg}$  with variable Wo reflects metastable crystallization.
3. Olivine compositions in most diabases reflect reaction with residual liquid and define a trend of Fe enrichment toward the top of the sills. Fayalite occurs in late Fe-rich pegmatitic diabase. Olivine phenocrysts in chill zones are in equilibrium with the liquid.
4. Plagioclase is the liquidus phase throughout the diabase. Maximum An in chilled margins ( $An_{71}$ ) indicates a liquidus  $T$  of 1110°C. Plagioclase shows an enrichment in Na toward the top of sill sections.
5. Crystallization sequences of the mafic minerals in the Nipigon diabase are sensitive indicators of silica activity. Differences in silica activity may relate to degree of contamination with crustal material.

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