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# Clinopyroxenes from the Keweenawan Lavas of Minnesota

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## Abstract

The Keweenawan (Late Precambrian) lava flows in northern Minnesota include the volcanic series: tholeiitic olivine basalt, basaltic andesite, quartz latite, and rhyolite, which is assumed to be derived from a tholeiitic parental magma. These lavas contain calcic clinopyroxene which ranges from $Ca_{44}Mg_{45}Fe_{11}$ to $Ca_{43}Mg_{12}Fe_{45}$. The crystallization trend of these clinopyroxenes is characterized by marked iron enrichment and is similar to that of the associated Beaver Bay Gabbro Complex and of the Skaergaard Intrusion. The mineral assemblage of olivine + ferroaugite + quartz and the crystallization trend of the ferroaugites are characteristic of equilibrium crystallization of pyroxene during the late stage of differentiation of tholeiitic magma.

## Introduction

The compositional trends and the phase relations of pyroxenes in intermediate and felsic volcanic rocks of tholeiitic derivation have been reported by many investigators (*e.g.*, Carmichael, 1960; Kuno, 1969; Emeleus, Dunham, and Thompson, 1971). One such rather complete series of lavas of generally tholeiitic affinities is the North Shore Volcanic Group of Late Precambrian age, about 1130 million years old, which underlies (Fig. 1) most of the shore of Lake Superior in northeastern Minnesota, U.S.A. (Green, 1972). This series, which includes approximately 7500 meters (25,000 feet) of lavas, contains some types which are more potassic than is typical in pure tholeiitic suites, and it ranges in composition from olivine tholeiites through quartz tholeiites, basaltic andesites, trachybasalts, andesites, and quartz latites to rhyolites. The olivine tholeiites are the most abundant single rock type. The flows are intruded by the immense Duluth Gabbro Complex and by locally abundant shallow intrusive rocks, principally olivine diabase. The Beaver Bay Complex, described by Grout and Schwartz (1939) and Green (1972) and in part by Gehman (1957) is one such group of intrusions. Muir (1954) and Konda (1970) have studied the clinopyroxenes of the Beaver Bay Complex. Except for lavas and gabbro far to the northeast and southwest of those considered here, all of the rocks (including the Beaver Bay Complex) which intrude the North Shore Volcanic Group are within ±15 m.y. of the same age as the lavas (Silver and Green, 1972), show the same magnetic pole position (Beck and Lindsley, 1969; Books, 1972; Books and Green, 1972) and are assumed to be cogenetic with the lavas.

The basalts of the North Shore Volcanic Group are nearly all non-porphyritic, the pyroxenes occurring generally either as poikilitic crystals in ophitic or subophitic intergrowth with plagioclase or as small equant crystals in an intergranular texture. The intermediate and felsic lavas, however, are nearly all porphyritic, with small plagioclase, clinopyroxene, and commonly also magnetite and olivine phenocrysts. The olivine has in all cases been destroyed by secondary alteration, but the clinopyroxene is fresh in many rocks.

To understand the complete trend of compositions of the clinopyroxenes during fractionation of tholeiitic magma, partial analyses of many crystals from this volcanic series were obtained using an electron microprobe (Green), and the clinopyroxenes from four large samples were separated and analyzed by conventional wet chemical methods (Konda).

The samples studied for this report are from lava flows of the uppermost 2000 meters of the North Shore Volcanic Group, plus a dike that crosscuts the flows roughly 2600 meters from the top of the exposed section. The sample localities are shown on Figure 1. This paper presents the results of these analyses and discusses the petrologic significance of the pyroxene crystallization trend thus outlined.

## Petrography

Chemical analyses of most of the rocks sampled are given in Green (1972); they are plotted on an *AFM* diagram in Figure 2. Brief petrographic descriptions of the rocks from which pyroxenes were studied follow.

(a) Olivine basalt (T-56): lakeshore at E. edge sec. 12, T.59N., R.4W. Slightly porphyritic, fine- to medium-grained basalt flow between 7–8 m thick (Fig. 3A). Major minerals: clots of small, euhedral bytownite phenocrysts zoned $An_{85}$-$An_{60}$; poikilitic augite up to 2 mm across enclosing small labradorite laths; subhedral olivine now completely altered to serpentine or chlorite; and both ilmenite and Ti-magnetite. This basalt is the most "primitive" (highest Mg/Fe ratio, lowest $K_2O$) of the olivine tholeiites analyzed in the North Shore Volcanic Group, and, according to calculations by Phinney (1970), it may be close to the parental magma composition for the Duluth Gabbro Complex as well as for the North Shore Volcanic Group.

(b) Olivine basalt (T-22); on old road, NW 1/4 sec. 2, T.58N., R.5W. Medium-grained, subophitic; the upper-central part of a very thick flow. About 3 percent small olivine crystals, completely altered; augite up to 3 mm diam., some as skeletal intergrowths with plagioclase; both ilm. and Ti-mag; plagioclase laths zoned, $An_{65}$-$An_{20}$. Trace of interstitial granophyre. Saponite and zeolites fill diktytaxitic cavities.

(c) Ophitic olivine basalt (DY-3): lakeshore at north edge of Sec. 15, T.60N., R.2W. The lower

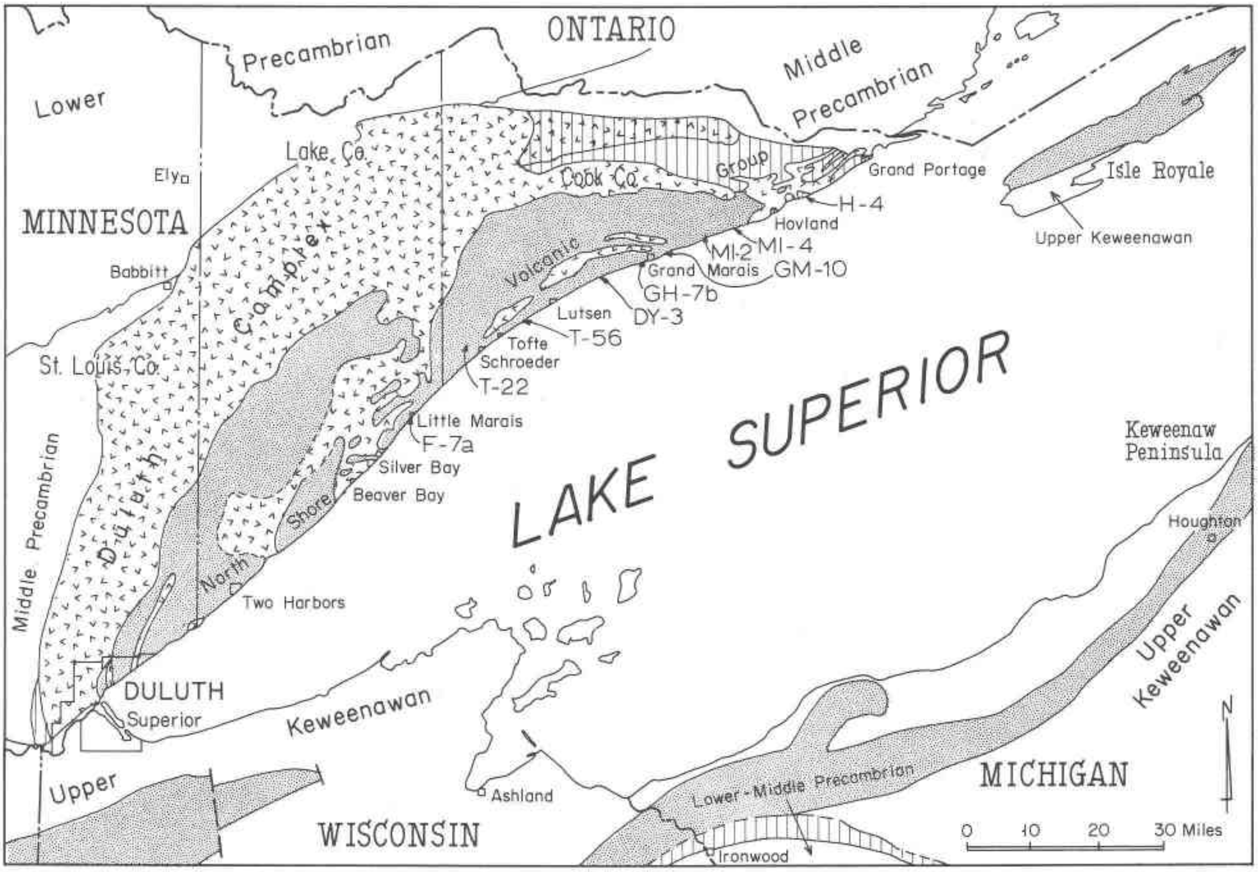

FIG. 1. Generalized geologic map of Keweenawan rocks in the western Lake Superior area showing location of samples studied. Check pattern, intrusive rocks; vertical ruling, Lower Keweenawan rocks (magnetically reversed); stippled, Middle Keweenawan lavas (magnetically normal). After Green (1972, Fig. V-3).

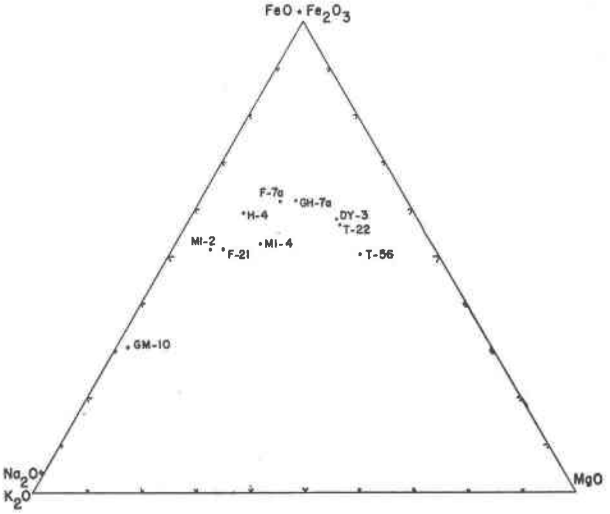

FIG. 2. *AFM* diagram for rocks from which pyroxene analyses are given in this paper. Point labelled GH-7a is derived from rock analysis S & G-5-9 (from the same flow but a different locality), and point DY-3 is derived from rock analysis DY-6b (from a similar flow slightly lower in the section than DY-3). Rock analyses from Green (1972).

middle part of a very thick (200 m) flow of fine- to medium-grained basalt. Tabular plagioclase predominates, with fresh ophitic augite, olivine pseudomorphs, magnetite and ilmenite (Fig. 3B). Interstitial cavities contain zeolites and calcite.

(d) Porphyritic basalt (GH-7A): lakeshore 500 m west of power plant at Grand Marais; SE 1/4 SW 1/4 Sec. 20, T.61N., R.1E. The chilled base of a thick (110 m) basaltic to andesitic sheet that is probably a flow but may be a sill. Abundant 1–2 mm phenocrysts of zoned plagioclase, about 2 percent of fresh prismatic augite crystals (0.5–1.5 mm) and fewer small altered olivine phenocrysts set in a subspherulitic, fine-grained groundmass of plagioclase tablets, clinopyroxene prisms, and magnetite blocks, with interstitial alkali feldspar in the coarser areas. Original small miarolitic cavities filled with quartz and an oxidized chloritic mineral.

(e) Porphyritic basaltic andesite (F-7a): lakeshore, NE 1/4 Sec. 21, T.57N, R.6W. The basal, chilled portion of a very thick (at least 100 m) flow. Red-brown, fine-grained potassic basaltic andesite with 10 percent small phenocrysts of plagioclase ($An_{55}$), augite, rare pigeonite, and olivine (Fig. 3C). The olivine phenocrysts (completely altered to iddingsite) are prismatic and some are in parallel intergrowth with augite. Augite phenocrysts euhedral, pale green, nonpleochroic. A few show marginal zoning by changes in extinction angle and birefringence. Some augite shows very thin exsolution lamellae (pigeonite?). Groundmass intergranular in texture, with plagioclase, alkali-feldspar, augite, pigeonite, opaques, and greenish clay minerals. The pigeonite tends to be oxidized along rims and fractures.

(f) Basaltic andesite (MI-4): lakeshore, SE 1/4 Sec. 22, T.62N., R.3E. Fine-grained red-brown aphyric andesite or trachy-andesite flow showing thin oxidation banding. Intergranular to intersertal texture with small plagioclase laths (An 53-45), magnetite octahedra, and 8 percent blocky, fresh ferroaugites in a groundmass of oxidized glass, magnetite, alkali-feldspar, quartz, and amphibole (Fig. 3D). Cavities are filled with quartz, chlorite, clay, and zeolites. Flow thickness unknown.

(g) Porphyritic andesite or trachyandesite (H-4): Highway 61, center line Sec. 12, T.62N, R.4E. Very fine-grained, dark brown dike, which transects the lavas about 2600 m below the top of the exposed section. About 3 percent of small phenocrysts of subhedral oligoclase ($An_{25}$), ferroaugite, and magnetite, in a groundmass of plagioclase, alkali-feldspar, ferroaugite, magnetite, anhedral hornblende, possible devitrified brown glass, and alteration products.

(h) Porphyritic intermediate quartz latite (MI-2): Highway 61 at W. edge Sec. 6, T.62N., R.3E. Fifty m-thick lava flow rather similar to rocks termed "icelandites" by Carmichael (1964). Reddish brown, fine-grained; about 7 percent of small phenocrysts of stout tabular, unzoned andesine ($An_{40}$), ferroaugite, altered olivine, and magnetite. The ferroaugite phenocrysts are fresh, about 1 mm across; some are aggregated with the other phenocrysts (Fig. 3E). The groundmass minerals are plagioclase, alkali-feldspar, interstitial quartz, opaques, and green alteration products, probably chlorite. Although there may have been clinopyroxene in the groundmass, it is not now recognizable.

(i) Porphyritic rhyolite (GM-10): lakeshore, center line Sec. 14, T.61N, R.1E. Basal spherulitic zone of a rhyolite lava flow that is as much as 155 m thick. Orange-red, aphanitic, about 3 percent small blocky phenocrysts of plagioclase ($An_{35-26}$) and rare quartz, ferroaugite, magnetite and altered olivine. The ferroaugite occurs as small, fresh, subhedral phenocrysts (0.1 × 0.8 mm) (Fig. 3F). Groundmass microcrystalline feldspar and quartz with minute opaque grains.

(k) Porphyritic intermediate quartz latite (F-21): NE 1/4 Sec. 28, T.57N., R.7W. Red-brown, very fine-grained "andesite" assumed to be a lava although contacts not exposed. Contains 10 percent small, blocky albite phenocrysts, about 3 percent spongy augite prisms and about 2 percent each of magnetite and oxidized olivine. Groundmass dominated by K-feldspar, with lesser amounts of plagi-

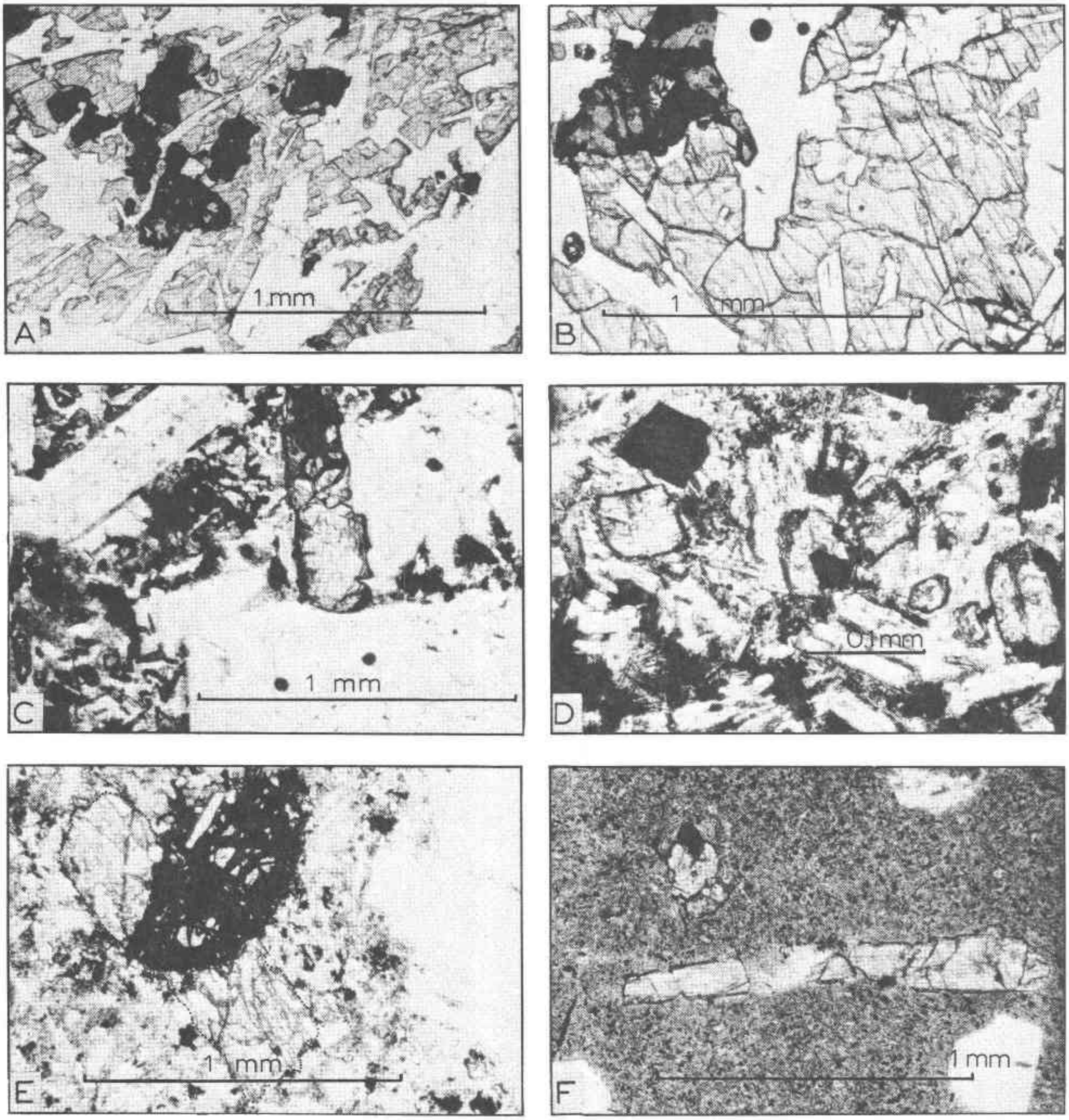

FIG. 3. Photomicrographs of clinopyroxenes in Keweenawan Lavas. **A**, ophitic augite enclosing plagioclase and pseudomorphs of olivine in olivine tholeiite T-56; **B**, ophitic augite enclosing plagioclase with olivine pseudomorph in olivine tholeiite DY-6b (flow close to and similar to pyroxene sample DY-3); **C**, augite and plagioclase phenocrysts, olivine pseudomorph in basaltic andesite F-7a; **D**, equant augite crystals with magnetite and plagioclase in andesite MI-4; **E**, prismatic ferroaugite, plagioclase, and olivine-pseudomorph phenocrysts with abundant apatite in intermediate quartz latite MI-2; **F**, prismatic ferroaugite, plagioclase, and small magnetite phenocrysts in rhyolite (felsic quartz latite) GM-10.

oclase, quartz, yellow-green secondary minerals, apatite, magnetite, and ilmenite.

## Analytical Results

The clinopyroxene phenocrysts of three large samples and subophitic augite of a fourth were separated, using the isodynamic separator and Clerici's solution, and analyzed by conventional wet chemical methods (Konda). Groundmass pyroxenes in the porphyritic rocks either were not present (MI-2) or were avoided by size classification during separation. In addition, about forty partial analyses (for Mg, Fe, Ca) of pyroxenes from six other lavas described above were obtained by Green using the MAC electron microprobe at the Department of Geology and Geophysics at the University of Minnesota, Minneapolis, with the assistance of Paul W. Weiblen, who also analyzed the pyroxene from the rhyolite GM-10. The standards for microprobe analyses were pyroxenes analyzed by wet chemical methods. The results of the wet chemical analyses are shown in Table 1, and the Mg/Fe/Ca relations of all analyzed pyroxenes are shown in Figure 4.

A weak zoning in the ophitic pyroxenes of the olivine tholeiites T-56 and DY-3 is suggested, trending away from diopsidic and toward subcalcic compositions with a slight increase in iron content. The compositional variation within the pyroxenes from saturated, intergranular basalts and basaltic andesites (*e.g.* MI-4) is mostly in Mg/Fe ratio, nearly parallel to the Di-Hd join. The ferroaugites of the intermediate quartz latite, MI-2, show enrichment in both Ca and Fe at the margin, and the quartz latite F-21 shows principally Mg/Fe zoning. Microprobe study of the clinopyroxene from rhyolite GM-10 showed no zoning present.

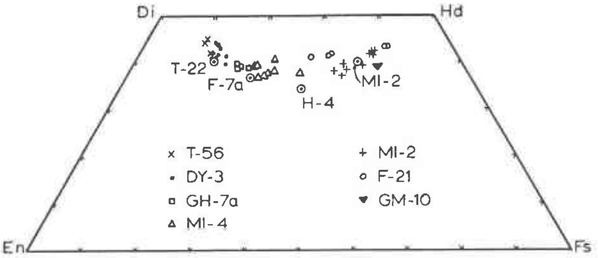

FIG. 4. Atomic ratios of analyzed calcic clinopyroxenes on pyroxene quadrilateral. Points shown by circle around dot are wet-chemically analyzed (Table 1); others are individual point analyses by electron microprobe, except GM-10 which is the average of 4 points on each of two grains. All are phenocrysts except T-56 and DY-3 (poikilitic augite), T-22 (subophitic augite), MI-4 (equant groundmass pyroxene).

TABLE 1. The Chemical Compositions and Atomic Ratios of Calcic Clinopyroxenes from Keweenawan Flows, North Shore Volcanic Group, Minnesota

*T. Konda, Analyst (wet chem.)*

| | 1 | 2 | 3 | 4 | | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 50.74 | 51.00 | 46.54 | 48.14 | Si | 1.880 | 1.923 | 1.852 | 1.916 |
| $TiO_2$ | 1.16 | 0.93 | 0.82 | 0.80 | $Al_{IV}$ | 0.120 | 0.077 | 0.101 | 0.061 |
| $Al_2O_3$ | 2.98 | 3.18 | 2.18 | 1.31 | Ti | ----- | ----- | 0.024 | 0.023 |
| $Fe_2O_3$ | 2.05 | 2.59 | 1.52 | 1.40 | $Fe^{+3}$ | ----- | ----- | 0.023 | ----- |
| FeO | 7.34 | 10.65 | 19.22 | 22.40 | $Al_{VI}$ | 0.010 | 0.064 | ----- | ----- |
| MnO | 0.16 | 0.29 | 0.37 | 0.47 | Ti | 0.032 | 0.026 | ----- | ----- |
| MgO | 15.53 | 13.08 | 10.91 | 6.26 | $Fe^{+3}$ | 0.057 | 0.073 | 0.022 | 0.041 |
| CaO | 19.66 | 16.58 | 16.09 | 18.37 | $Fe^{+2}$ | 0.227 | 0.336 | 0.630 | 0.745 |
| $Na_2O$ | 0.57 | 0.64 | 0.60 | 0.25 | Mn | 0.003 | 0.009 | 0.012 | 0.041 |
| $K_2O$ | 0.09 | 0.17 | 0.28 | 0.26 | Mg | 0.858 | 0.736 | 0.642 | 0.371 |
| $H_2O(+)$ | 0.45 | 0.86 | 0.84 | 0.53 | Ca | 0.780 | 0.670 | 0.685 | 0.783 |
| $H_2O(-)$ | 0.10 | 0.34 | ----- | ----- | Na | 0.040 | 0.047 | 0.045 | 0.019 |
| $P_2O_5$ | 0.00 | 0.01 | 0.20 | 0.40 | K | 0.004 | 0.005 | 0.013 | 0.013 |
| | | | | | P | ----- | ----- | 0.006 | 0.013 |
| Total | 100.83 | 100.32 | 99.57 | 100.59 | Z | 2.000 | 2.000 | 2.000 | 2.000 |
| | | | | | WXY | 2.011 | 1.967 | 1.991 | 1.999 |
| | | | | | Atomic % | | | | |
| | | | | | Ca | 40.5 | 36.7 | 34.4 | 40.1 |
| | | | | | Mg | 44.6 | 40.4 | 32.2 | 19.0 |
| | | | | | Fe* | 14.9 | 22.9 | 33.4 | 40.9 |
| | | | | | $(Fe^{*}=Fe^{+2}+Fe^{+3}+Mn)$ | | | | |

1. Augite from coarse olivine basalt (T-22)
2. Augite phenocrysts from basaltic andesite (F-7a)
3. Ferroaugite phenocrysts from augite andesite (H-4)
4. Ferroaugite phenocrysts from intermediate quartz latite (MI-2)

## Discussion

Figure 5 shows the correlation between the atomic Fe/(Fe+Mg) ratios of the clinopyroxenes and the ratio of total FeO to total FeO+MgO in the analyzed host lavas. Figure 6 shows the pyroxene Fe/(Fe+Mg) ratio plotted against $SiO_2$ content of the host rock. Because the percentage of pyroxene phenocrysts in the porphyritic lavas is very small, the whole-rock Fe/Mg ratios do not depend greatly on the pyroxene phenocryst compositions. Consequently, the general correlations shown in Figures 5 and 6 can be interpreted as indicating that the pyroxene phenocryst compositions were controlled by the compositions of the lavas in which we now find them. Thus, the phenocrysts were probably indigenous, and not included xenocrysts.

The clinopyroxenes in samples F-7a, GH-7a, and H-4 show slightly low Fe/(Fe+Mg) ratios (Fig. 5) as compared to the general trend. Under the microscope, these rocks contain small amounts of phenocrystic magnetite, suggesting that the magnetite may have precipitated during or before the crystallization of clinopyroxene and prevented further iron enrich-

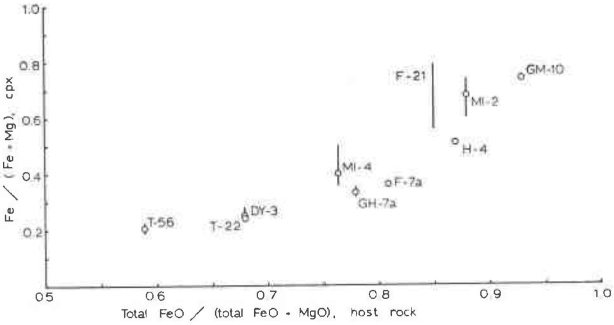

FIG. 5. Atomic Fe/(Fe+Mg) of clinopyroxenes plotted against total FeO/(total FeO+MgO) (wt. percent) of host rocks. Augite DY-3 is compared with analyzed DY-6b, a similar flow slightly lower in the section. Augite GH-7a is compared with analyzed rock S & G-59 from another locality in the same flow. Rock analyses from Green (1972).

ment in the pyroxene. Although Eggler and Burnham (1973) find that magnetite should not occur at the liquidus in andesitic magmas, it evidently did start to precipitate in these lavas at some time during the first 10 to 20 percent of crystallization. However, there is less magnetite than pyroxene present as phenocrysts in these rocks, and there is no evidence to indicate that it started to crystallize before the clinopyroxene. Furthermore, these samples have no more magnetite as phenocrysts than the samples falling on the "general trend." The relatively low Fe/(Fe+Mg) ratios of these three clinopyroxenes compared to their host rocks may be a reflection of the fact that their small content of pyroxene phenocrysts represents only the first, most magnesian part of their normative pyroxene content; whereas in MI-4, an aphyric andesite, the analyzed pyroxene is in the groundmass and should more nearly approach the normative values. In the three more felsic samples (F-21, MI-2, GM-10) the analyzed phenocrysts probably contain most of the potential pyroxene in the rock.

Also, these three intermediate samples GH-7a, F-7a, and H-4 show a high content of magnetite in the groundmass as compared to the other rocks, which would increase the total FeO/(FeO+MgO) total ratio of the rock analysis.

The compositional zoning of these clinopyroxenes (Fig. 4) is similar to the pyroxene trend direction observed in many layered intrusions (*e.g.*, Skaergaard and Beaver Bay), and although these rocks are obviously lavas, the basaltic groundmass pyroxenes analyzed do not show any "quench trend" referred to by Muir and Tilley (1964) or Smith and Lindsley (1971). We interpret this lack of a "quench trend" to be the result of relatively slow crystallization of these thick, flood basalts. Slow crystallization is also indicated by their relatively coarse grain size and their flat surfaces and wide extent. The observed trend is instead inferred to be the "intratelluric equilibrium trend" referred to by Muir and Tilley.

Clinopyroxenes from the consanguineous Beaver Bay Complex have been studied by Muir (1954) and more recently by Konda (1970) and Stevenson (1973, 1974). Because the pyroxene phenocrysts in the lavas could be expected to have formed during hypabyssal differentiation under conditions similar to those obtaining during crystallization of the Beaver Bay intrusive rocks, it is interesting to compare the clinopyroxenes of the lavas with those of the Beaver Bay Complex. Although the lava samples described in this paper came from a much wider area than the Beaver Bay Complex (Fig. 1), the controls on and character of differentiation of both may well have been similar. Some of the sampled lavas may actually have been surface extrusions of the same magmas that produced parts of the Beaver Bay Complex, although it would be difficult to demonstrate such a relationship.

In chemical characteristics, the clinopyroxenes from the lavas of the North Shore Volcanic Group are slightly richer in $Al_2O_3$ and $Na_2O$, but have about the same amount of MnO and $TiO_2$ as those of similar Fe/Mg ratio from the Beaver Bay Complex (Konda, 1970). The wet chemical analyses of Table 1 show that the CaO contents of the clinopyroxenes from most of the lava flows are slightly

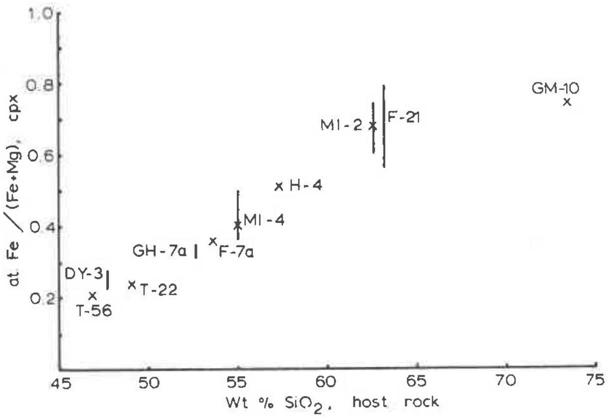

FIG. 6. Atomic Fe/(Fe+Mg) of calcic clinopyroxenes plotted against weight percent $SiO_2$ in host rocks.

lower than those from the Beaver Bay intrusion (Fig. 7). This might indicate slightly higher temperatures of crystallization for the phenocrysts of the lavas than for the intrusive rocks. However, microprobe analyses of clinopyroxenes from DY-3, F-21, and MI-4 (Fig. 4) show essentially the same or lower CaO content compared to those from the Beaver Bay Complex, and the two populations would be difficult to distinguish.

The crystallization trends of the clinopyroxenes in the Keweenawan flows and the cumulus augites in the Beaver Bay Complex are similar, as shown in Figure 7. However, in the Beaver Bay Complex, Konda (1970) shows that the calcic clinopyroxenes are locally rimmed by pigeonite-ferropigeonite, which is inferred to have crystallized by the reaction between cumulus Ca-rich clinopyroxenes and the interstitial liquid. On the other hand, the calcic clinopyroxenes from the related flows (this paper) do not have such a mantle of Ca-poor pyroxene, probably because such a reaction point had not been reached when the lavas were extruded and quenched. As mentioned above, the potential Ca-poor (and Fe-rich) pyroxene components probably remain in the unanalyzed groundmass ferromagnesian minerals.

Figure 7 further shows for comparison the trend of clinopyroxene compositions for a variety of Tertiary and Quaternary volcanic rocks (Carmichael, 1967); it is essentially identical to that of the analyzed Keweenawan pyroxenes. From a study of the associated oxide minerals, Carmichael (1967) infers pyroxene crystallization temperatures ranging from 970° to 915°C for similar intermediate and felsic porphyritic lavas.

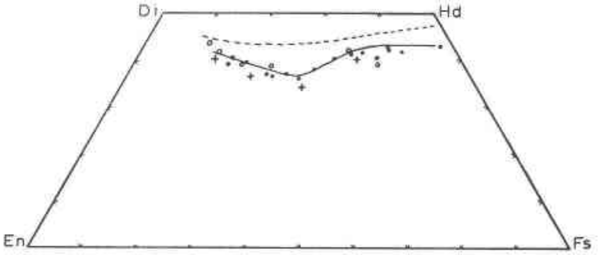

FIG. 7. Calcic pyroxene trends compared. Crosses, wet-chemically analyzed clinopyroxenes from Keweenawan lavas; circles, average compositions of clinopyroxenes from Keweenawan lavas analyzed by microprobe; dots, analyzed pyroxenes from Beaver Bay complex (Konda, 1970); solid line, trend of clinopyroxenes from various Tertiary and Quaternary volcanic rocks (Carmichael, 1967); dashed line, trend of clinopyroxenes from Shiant Isles sill (Gibb, 1973).

The assemblage of mafic minerals present is closely related to the crystallization trend of pyroxenes at the late stages of fractionation, as suggested from experimental work (Lindsley and Munoz, 1969) and from natural rocks (Kuno, 1969; Emeleus *et al*, 1971). The most common phenocryst assemblages of the mafic minerals in the analyzed samples are as follows: augite + olivine in basalt (early stage; no phenocrysts); augite + olivine phenocrysts in basaltic andesite (GH-7a); augite + pigeonite + olivine + magnetite in basaltic andesite (F-7a); ferroaugite + olivine + magnetite in intermediate quartz latite (MI-2); and ferroaugite, olivine, and magnetite in rhyolite (GM-10) at a late stage. Ferroaugite phenocrysts from MI-2 and GM-10 have Fe/(Fe+Mg) ratios of 0.63–0.73, which are similar to those of ferroaugite from porphyritic felsite and granophyre in Scotland (Emeleus *et al,* 1971, no. 8 of group 3 and nos. 5a, 5b of group 4, Table 2). However, the mineral assemblages are different: ferroaugite + olivine in the Keweenawan lavas, and ferroaugite + ferro-pigeonite in the Scottish felsic rocks.

Based on the experimental work of Lindsley and Munoz (1969, p. 316), the reaction Ferrosilite = Fayalite + $SiO_2$ melt is such that an increase in the activity of $SiO_2$ leads to an increase in the activity of Fs under equilibrium conditions. Persistence of olivine throughout the crystallization sequence and a higher content of alkalies in these Keweenawan lavas than in the typical tholeiitic suites and Scottish felsic rocks indicate the magma compositions to be slightly sub-alkaline and suggest a slightly low $SiO_2$ activity. However, the Keweenawan trends clearly differ from that of the mildly alkaline Shiant Isles sill (Gibb, 1973), which is more calcic and lacks the central dip in Ca content (Fig. 7). Although $SiO_2$ activity is close to unity near the solidus for each Keweenawan lava, it would appear that $SiO_2$ activity did not increase fast enough below the liquidus to stabilize Ca-poor pyroxene. On the other hand, however, Mg/Fe distribution values between coexisting ferropigeonite (5c, group 4) and ferroaugite (5a and 5b, group 4) in the granophyres of Scotland are somewhat variable, possibly suggesting metastable crystallization of ferropigeonite in the Scottish granophyre. Also, from the descriptions of the ferropigeonite-bearing rocks (Emeleus *et al,* 1971, p. 941–944), the crystals are rather variable in composition within individual samples and some show complex zoning. This too would suggest that the ferropigeonites described result from disequilibrium crystallization, perhaps related to an extension of Muir and Tilley's "quench trend" (1964). The present data agree with experiments by Smith (1971) on compositions along the join $Fs_{85}En_{15}$–Wo. These indicate that the assemblage calcic clinopyroxene—fayalitic olivine—silica is stable at low crustal pressures and temperatures of 1000° to 800°C.

The stable mineral assemblage during late stages of fractionation appears to be ferroaugite + fayalitic olivine + quartz, and the crystallization trend shown in Keweenawan lavas MI-2 and GM-10 would be representative of the late-stage stable crystallization trend of pyroxenes in tholeiitic magma under hypabyssal conditions.

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