# CLINOPYROXENES OF ALKALI OLIVINE-BASALT MAGMA

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### Abstract

In representatives of alkali olivine-basalt magma, as contrasted to tholeiitic rocks, only one common pyroxene, a clinopyroxene close to diopside or salite, appears. The clinopyroxene crystallization trend is parallel to the Di-He join, principally in the fields of diopside or salite. Analytical data indicates that alkali olivine-basalt clinopyroxenes having compositions more iron-rich than  $Ca_{4b}Mg_{2b}Fe_{30}$  must be comparatively rare.

The contrasting behavior of the pyroxene assemblage of alkali olivine-basalt and tholeiitic magma depends principally on the undersaturated or saturated nature of the respective residual magmatic solutions, which determine whether or not orthopyroxene as a product of magmatic reaction with early-formed olivine will appear. The higher modal pyroxene content of tholeiites, their more varied pyroxene assemblage, and the greater variation in clinopyroxene composition with differentiation compared with alkali olivinebasalt clinopyroxenes, are important consequences of this reaction.

### INTRODUCTION

While much has been written on the crystallization trends and mutual relationships of clinopyroxenes from tholeiitic rocks, clinopyroxenes of under-saturated basic alkaline rocks have been comparatively neglected. Except for Murray's (1954) investigation of the Garbh Eilean clinopyroxenes, little attention has been directed to crystallization trends of clinopyroxenes from a single intrusion of alkali olivine-basalt type.

Several of the concepts in the present paper result from the investigation of the Black Jack teschenite sill, near Gunnedah, New South Wales. This differentiated five hundred foot thick intrusion of Tertiary age is a typical representative of alkali olivine-basalt magma. The principal mineralogical (modal) variations in the sill are expressed in a progressive decrease in olivine with increasing height above the lower contacts, while clinopyroxene and iron ore are slightly more abundant in the upper levels of the intrusion. During differentiation, the olivine becomes more fayalitic (Fa<sub>21</sub> to Fa<sub>60</sub>) while the plagioclase feldspar is enriched in albite (An<sub>72</sub> to An<sub>43</sub>) (Table 1). The homogeneous iron-titanium ores also reveal considerable compositional changes. In strong contrast, the associated bulk clinopyroxene (usually strongly zoned) undergoes little change in composition during differentiation (Ca48Mg37Fe15 to Ca47Mg34Fe19). The limits of clinopyroxene composition are close to the range, Ca49Mg37Fe14 to Ca47Mg33Fe20 (Table 2), based on analyses of the Mg- and Fe-rich fractions of the analyzed bulk clinopyroxene.

The writer follows Poldervaart and Hess (1951, Fig. 1B) on clinopyroxene nomenclature. The clinopyroxene compositions, except in certain instances where they have been derived from a previous source, are expressed in atomic percentages of Ca, Mg and Fe (following Hess, 1949). The following concepts are fundamental to any discussion dealing with

the nature and crystallization histories of the pyroxenes:

- (i) The recognition of certain magma types.
- (ii) Clinopyroxene nomenclature based on optical properties, allied with the use of optics for compositional purposes.

(i) The concept of magma types, proposed by the authors of the Mull memoir (Bailey *et al.*, 1924) is now well known. It is "a permanent contribution to petrologic thought" (Tilley, 1950, p. 38). In their definition of the Plateau and Non-Porphyritic Central magma types, the Mull authors (1924, p. 14) state that "a purple colour is characteristic of the augite" in the Plateau rocks. The highly calcic diopsidic nature of the clinopyroxene in the Mull Plateau (=olivine-basalt) magma, compared with the enstatite-augite varieties in the the Non-Porphyritic (=tholeiitic) magma type, was pointed out by Kennedy (1931, p. 63; 1933, pp. 240-241). Similar mineralogical differences had been recognized earlier by Washington (1922, p. 800) in the "cone-" and "plateau-basalts" respectively. The ambiguity arising from usage of the terms "olivine-basalt" and "tholeiite" as applied to magma types, has been discussed by Tilley (1950, pp. 40-41), who uses as an alternative for the former, the term "alkali olivine-basalt."

(ii) There is no analytical evidence indicating that the lime content (usually greater than 20 weight per cent) of clinopyroxenes from alkali olivine-basalt magma ever approaches that of pigeonite, as defined by Poldervaart and Hess (1951, p. 473), despite the fact that such pyroxenes may have low 2V's in the range 30-38 degrees (cf. Yagi, 1953, p. 780). Yet many writers, following Kuno (1936a, p. 141) have referred to these clinopyroxenes as "pigeonites" or "pigeonitic," with a consequent erroneous composition. The clinopyroxenes under discussion are usually richer in TiO2 (Table 2), Al2O3, Fe2O3 and CaO than common tholeiitic clinopyroxenes (see Hess, 1949, p. 633). There appears to be little agreement in the literature as to the exact variation in  $\gamma \wedge c$ , 2V, refractive indices, etc. to be ascribed to a particular constituent, whose presence in many cases cannot be diagnosed optically. The effects of TiO<sub>2</sub> on the optics are most uncertain (Dittler, 1929; Kuno, 1936; Segnit, 1953). The variable optics of the clinopyroxenes listed in Table 2 should be noted. Optical properties of titania-rich clinopyroxenes indicate a higher Fe and lower Ca content than revealed by analysis. Until other methods e.g. the correlation of cell dimensions with variation in Al3+, Fe3+, Ti4+ and Na+ (Kuno and Hess, 1953) become available, chemical analyses provide the safest means of deriving accurate compositions of titaniferous clinopyroxenes.

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### CLINOPYROXENE CRYSTALLIZATION TRENDS IN ALKALI Olivine-Basalt Magma

Hess (1941, pp. 574–578) summarized the work of Barth (1931; 1936), Tsuboi (1932) and Wager and Deer (1939) and drew up a course of crystallization for tholeiitic clinopyroxenes, a trend substantiated later by Edwards (1942) and Walker and Poldervaart (1949). The varying crystallization trends suggested by these workers are shown in Fig. 1. In certain cases it is clear that the suggested trends applied to clinopyroxenes from both tholeiitic and alkali olivine-basalt magmas.

Basic data on the crystallization trends of the clinopyroxenes from a



FIG. 1. Schematic representation of pyroxene crystallization trends in basic rocks. I Tsuboi (1932), followed by Kuno (1936a); II Barth (1936); III Wager and Deer (1939), integrating data from Kennedy (1933) and Kuno (1936a); IV Hess (1941, 1951).

single differentiated intrusion of alkali olivine-basalt type is now supplied by the Garbh Eilean and Black Jack pyroxenes. The principal compositional relationships of the main mineral series in the latter intrusion have already been summarized. In the former sill, the range in clinopyroxene composition is from  $Ca_{47}Mg_{42}Fe_{11}$ , the pyroxene in the picrite, to  $Ca_{44}Mg_{30.5}Fe_{25.5}$ , the iron-rich fraction of the clinopyroxene in the crinanite 325 feet above sea level (Murray, 1954, Table 1). In both intrusions, the modal olivine decreases with progressive magmatic evolution, a feature shown by other differentiated intrusions of this magma (Table 4). The olivines in the Garbh Eilean (Murray, 1954, Fig. 2) and Black Jack rocks are richer in ferrous iron and undergo considerably greater iron enrichment than the associated clinopyroxene. The crystallization trend of the latter minerals in both instances is parallel to the diopside-hedenbergite join (Fig. 2), principally in the fields of diopside and salite.



FIG. 2. Clinopyroxene crystallization trends in intrusions of alkali olivine-basalt type. Open circles—clinopyroxenes from the Black Jack sill, near Gunnedah, New South Wales trend AA'. Solid circles—clinopyroxenes from the Garbh Eilean sill, Shiant Isles, trend BB' (Murray, 1954).

One of the most striking features of the Garbh Eilean and Black Jack clinopyroxenes is their relatively small range in composition, for in this respect they lag strongly behind the associated minerals and parent rocks (see Murray, 1954, Fig. 3). Such relationships provide marked contrast to tholeiitic intrusions showing medium or strong fractionation, where the principal pyrogenetic minerals all undergo comparable compositional changes (Table 1).

To stabilize the trend indicated by the Garbh Eilean and Black Jack



FIG. 3. Compositions of titaniferous clinopyroxenes. Solid circles—clinopyroxenes from alkali olivine-basalt magma. Solid triangles—titaniferous clinopyroxenes from tholeiitic magma. Open circles—titaniferous clinopyroxenes from contaminated basic magma.

TABLE 1. COM	POSITIONAL VARIATION WI	THIN THE PRIJ	NCIPAL MINE	RAL SERIES OF S	OME DIFFERENTIATED INTR	RUSIONS
Intrusion	Clinopyroxene	Ortho- pyroxene	Olivine	Plagioclase	Remarks	Reference
Black Jack sill, Gunnedah, N. S. W.	Ca49Mg37Fe14 to Ca47Mg33Fe20	1	Fa21-Fa60	$\mathrm{An}_{72}\mathrm{-An}_{43}$	Olivine and feldspar com- positions refer to the cores of the crystals	
Garbh Eilean sill, Shiant Isles	Ca47M45Feu to Ca44Mg30.5Fe25.5		Fa17-Fa90	An <sub>80</sub> -An <sub>30</sub>	Upper composition limits of olivine and feldspar on zoned crystals	Johnston (1953) Murray (1954)
Skaergaard* intrusion East Greenland	Ca.16Mg3.2Fe1.2 to Ca.30Mg3Fe6.8	$Of_{40}-Of_{70}$	Fa <sub>34</sub> -Fa <sub>97</sub>	$\mathrm{An}_{60}\mathrm{-An}_{30}$		Wager and Deer (1939) Muir (1951)
New Amalfi sheet,* Mata- tiele	Wo36En47F517 to WO38En9F553	Of <sub>15</sub> -Of <sub>100</sub>	Fa15-Fa100	$\stackrel{An_{70}-An_{60}}{\rightarrow}(An_{31})$	Pyroxene composition from optics. Plagioclase (An <sub>al</sub> ) from upper faya- lite-hedenbergite-grano- phyre	Poldervaart (1944)
Palisade sill,*New Jersey	"hypersthene-augite to iron-rich pigeonite"	Of <sub>35</sub> -Of <sub>40</sub>	Fa <sub>20</sub> -Fa <sub>35</sub>	An <sub>7c</sub> -An <sub>48</sub>	Upper limit of olivine composition on zoned crystals	Walker (1940)
Mount Wellington* sill, Tasmania	${f Wo_{38}En_{60}ES_6}\ to to Vo_{20}En_{60}ES_5$ ${f Wo_{27}En_{48}ES_{25}};$ pigeonite ${f Wo_{10}En_{20}ES_{20}}$	Of <sub>15</sub> -Of <sub>30</sub>	rare	An <sub>75</sub> -An <sub>65</sub> →An <sub>56</sub> (outer zones)	Clinopyroxene composi- tions from optical meas- urements	Edwards (1942)
Dillsburg sill,* Penn,	Ca <sub>39</sub> Mg <sub>33</sub> Fe <sub>8</sub> to Ca <sub>43</sub> Mg <sub>16,5</sub> Fe <sub>40,5</sub>	1	Fa20-?	An <sub>70</sub> -An <sub>35</sub>	Clinopyroxene composi- tion from optics. Olivine rare	Hotz (1953)

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\* Products of tholeiitic magma.

minerals, additional clinopyroxenes have been plotted in Fig. 3. Since alkali olivine-basalt clinopyroxenes generally possess relatively high titania contents, attention was directed to clinopyroxenes containing more than average amounts of this constituent. Relevant pyroxene data concerning composition, optics and literature are listed in Table 2. The references in this table are not listed at the end of the paper.

The plotted analyses include nearly sixty clinopyroxenes from nontholeiitic igneous rocks (Table 2, Analyses 1–48). To save repetition, the Garbh Eilean clinopyroxenes (Murray, 1954, Table 1) have not been included in the tabulation. The parent rocks are undersaturated (alkalic) types, usually with olivine and/or feldspathoids, and include many representatives of alkali olivine-basalt magma. The debatable question of the possible genetic interrelationships of certain of the listed rocks is outside the scope of the present investigation.

The additional analyses include titaniferous clinopyroxenes from tholeiitic magma (Table 2, Analyses 49–53), and from basic feldspathoidal rocks produced by reaction of basic magma with carbonate sediments (Analyses 54–56).

The plot of the clinopyroxenes from basic alkaline magmas (Fig. 3) yields important results, especially when one considers the variation in age, location and most important, the magmatic histories of the parent rocks themselves. As a group, these minerals reveal little variation in composition. The majority plots in the field of salite; a small number fall in the augite field but close to the augite-salite boundary. There is an absence of any marked trend extending through ferrosalite to hedenbergite, only three analyses revealing significant iron enrichment (Table 2, Analyses 40 and 46; Murray, 1954, Table 1, Analysis 31 H).

The titaniferous clinopyroxenes from both tholeiitic and contaminated basic rocks plot outside the field of clinopyroxenes from alkaline rocks, the tholeiitic examples behaving in a manner similar to their titania-poor equivalents in differentiated tholeiitic magma, with appreciable replacement of both  $Ca^{2+}$  and  $Mg^{2+}$  by  $Fe^{2+}$ . The carbonate-basic magma reaction types in the three instances reveal lime enrichment.

Comparing Figs. 2 and 3, it is seen that the compositional trends of the Garbh Eilean and Black Jack clinopyroxenes embrace the normal compositional limits of alkali olivine-basalt clinopyroxenes, i.e. the trend is dominantly parallel to the diopside-hedenbergite join, within the field embraced by  $Fe_{9}$ - $Fe_{21}$  and  $Ca_{50}$ - $Ca_{43}$ . There is no tendency for a pyroxene trend from diopside to ferrosilite, a trend demonstrated in certain tholeiitic rocks (Kuno, 1955), but often considered to apply to basaltic magmas in general (Fig. 1).

Murray (1954, Fig. 1) has extended the crystallization course of the

LOTTED ON FIG. 3	Reference	edah, J. F. G. Wilkinson (1956), <i>Geol. Mag.</i> , (in press)		edah, <i>Gool. Mag.</i> , (in press)			'alde F. W. Clarke, (1910), U. S.	Geol. Surv., Bull. 419, 43 W. Cross, (1897), Am. J.	East E. A. Vincent, (1953),	0.1.6.S., 109, 34 H. S. Washington and H. E. Merwin (1021) A., 7 Sei	(Ser. 5), 1, 22 H. S. Washington, and H. E.	Merwin, <i>op. cit.</i> , 29 H. S. Washington, and H. E. Merwin, (1927), <i>Am. J. Sci.</i> ,	(Ser. 5), 14, 185 Dis- H. S. Washington, (1906),	Carnegie Publ. No. 57, 134 H. S. Washington, and H. E.	Merwin, (1925), Am. Min- erul., 8, 105 Fene- W. Kunitz, (1936), N. Jb.
US CLINOPYROXENES P.	Locality	Black Jack sill, Gunne N. S. W.		Black Jack sill, Gunn N. S. W.			Black Mountain, Uv	Quadrangle, Texas Leucite Hills, Wyomin	Skaergaard area,	Greenland Vesuvius	Monti Rossi, Etna	Villa Senni, Italy	Ticchiena, Hernican	trict, Italy Alban Hills, Italy	d'Almeida Barrarco, J
SITIONS OF TITANIFERO	Rock type	teschenite, 20 feet above lower contact (1) Mg-rich frac-	(2) Bulk clinopy-	roxene teschenite approx. 500 feet above lower contact	<ul><li>(3) bulk clinopy- roxene</li></ul>	(4) Fe rich frac-	uon nepheline-basalt	wyomingite	camptonite	leucite-tephrite	alkali-andesite (?)	missourite	leucitite	leucitite	syenite
C PROPERTIES AND COMPOS	Optical properties	$\beta = 1.704 - 1.704$ $\beta = 1.704 - 1.708$	y=1.725-1.731	$\begin{array}{c} zv = 44-52; \gamma/c \ 42-45\\ \alpha = 1.699-1.707\\ \beta = 1.704-1.711\\ \gamma = 1.725-1.732\\ \gamma \tau = 0.50\\ \gamma \tau = 0$	$\sqrt{2} = 49-39; \gamma/\sqrt{6} 42-43$		I	1	$\alpha 1.690 \ \beta 1.698 \ \gamma 1.720$	$\beta 1.700-1.711 \gamma \wedge c = 45$	$\alpha 1.704 \ \beta 1.711 \ \gamma 1.732$	$\alpha 1.699 \ \beta 1.718 \ \gamma 1.742$ 2V = 66-67; $\gamma \wedge c \ 46$	I	$lpha 1.703 \ \beta 1.710 \ \gamma 1.727$	$\alpha 1.714 \gamma 1.740 \gamma \bigwedge _{c47}$
ABLE 2. OPTICAI	Composition in atom per cent	Ca49Mg37Fe14	$\mathrm{Ca_{48}Mg_{37}Fe_{15}}$	Ca47Mg34Fe19	;	Ca47Mg33Fe20	$\mathrm{Ca_{51}Mg_{37}Fe_{12}}$	Ca46Mg49Fe5	$\mathrm{Ca_{46}Mg_{42}Fe_{12}}$	$\mathrm{Ca_{45}Mg_{43}Fe_{12}}$	Ca48Mg41Fe11	Ca50Mg34Fe16	Ca43Mg38Fe19	$\mathrm{Ca_{51}Mg_{36}Fe_{13}}$	Ca48Mg37Fe15
T	Weight per cent TiO <sub>2</sub>	3.04	3.21	2.42		2.15	4.28	3.03	1.67	1.52	2.11	2.86	2.85	1.19	3.78
	Analysis number	1	2	3		4	Ŋ	9	7	8	6	10	11	12	13

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Reference	W. Kunitz, op. cit.	W. Kunitz, op. cit.	W. Kunitz, op. cit.	W. Kunitz, op. cit. W. Kunitz, op. cit.	W. Kunitz, op. cil. C. O. Hutton, (1943), Trans. Proc. Roy. Soc. N. Z., 72, 354	C. O. Hutton, (1942), Trans. Proc. Roy. Soc. N. Z., 72, 182	Th. G. Sahama, (1952), Am. I. Sci (Bowen Vol.), 466	F. Walker, and L. O. Nico- laysen, (1954), Col. Geology and Min. Res. 4, 19	C. H Warren, J. A. Allen, and M. F. Connor, (1917), Am. J. Sci. (Ser. 4), 43, 77	R. Brauns, (1928), N. Jb. Mim., Abt. A, 57, 133	R. Brauns, op. cit.	P. Esenwein, (1929), Zeils. Valk., 12, 120	L. Jugovics, (1934), M.A., 6,	X. Galkin, (1910), N. Jb. Min., 29, 687
Locality	Lobauer Berg	Kaiserstuhl	Meiches	Tenerife Los Siete, Funentes	Stöffelskuppe Brocken Ra., Eastern Wel- lington, N. Z.	L. Waihola, Otago, New Zealand	Nyamunuka Crater, S. W. Uganda	Mauritius	Ice River, Brit. Columbia	Laacher See, Rhineland	Gleeser Feld, Laacher See, Rhineland	Azores	Mount Medves, Hungary	Liebhards, Rhön
Rock type	"nepheline-doler-	phonolite	nephelinite	tephrite nepheline rock	nepheline-basalt teschenite	theralite	potash ankaratrite	dolerite with nephe- line and analcime	"Augitite" assoc. with nepheline-sy- enite	leucite-nepheline- basanite	alkali trachyte	atlantite (?)	"basalt-tuff"	lamprobolite-bear- ing basalt
Optical properties	$\alpha 1.719 \gamma 1.745$ $2V = 46 \sim 4.647$	$\alpha 1.716 \gamma 1.742$ $\gamma V = 58 \sim 5.748$	$\alpha 1.724 \gamma 1.752$ $2V = 46 \gamma \Lambda c 52$	$\alpha_{1.731}^{\alpha_{1.728}} \gamma_{1.758}^{\gamma_{1.728}} \gamma_{1.758}^{\gamma_{1.758}}$	$\alpha 1.712 \gamma 1.740$ $\alpha 1.690 \beta 1.697 \gamma 1.715$ $2V = 52-54 \gamma / c 42$	$\substack{\alpha 1.698 \ \beta 1.704 \ \gamma 1.724 \\ 2V = 48-63 \ }$	$\alpha 1.695 \ \beta 1.701 \ \gamma 1.721 \ 2V = 60 \sim \Lambda c46$	$\beta 1.696 2V = 48$	$lpha$ 1.725 $\gamma$ 1.746 $\gamma \wedge c$ 42	$\gamma \wedge c46.5 2E = 86$	1	$\alpha 1.704 \gamma 1.729 2V = 54 \gamma 0.45$	$2V = 57 \gamma \sqrt{c45} - 47$	I
Composition in atom per cent	Ca48Mg37Fe16	Ca48Mg38Fe14	Ca47Mg36Fe17	Ca45Mg39Fe16 Ca47Mg36Fe17	Ca49Mg37Fe14 Ca45Mg41Fe14	Ca50Mg32Fe18	Ca48Mg43Fe9	Ca47Mg38Fe15	Ca <sub>51</sub> Mg <sub>34</sub> Fe <sub>15</sub>	Ca52Mg40Fe8	Ca <sub>51</sub> Mg <sub>39</sub> Fe <sub>10</sub>	Ca43Mg47Fe10	$\mathrm{Ca_{50}Mg_{36}Fe_{14}}$	Ca48Mg36Fe16
Weight per cent TiO <sub>2</sub>	4.09	3.57	4.62	1.67 5.02	2.83 2.05	2.88	2.25	2.49	4.84	2.78	2.91	2.06	1.87	2.05
Analysis number	14	15	16	17 18	19 20	21	22	23	24	25	26	27	28	29

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Analysis number	Weight per cent TiO <sub>2</sub>	Composition in atom per cent	Optical properties	Rock type	Locality	Reference
30	1.24	Ca48Mg37Fe15	1	lamprobolite-bear- ing basalt	Gehulfensberg, Rhön	X. Galkin, op. cit.
31	1.44	Ca46Mg38Fe16	l	lamprobolite-bear-	Sparbrod, Rhön	X. Galkin, <i>op. cit</i> , 688
32	2.09	$\mathrm{Ca_{46}Mg_{41}Fe_{13}}$	$2V = 61 \gamma \wedge c43$	phenocrysts in ther-	Bo Ploi, Siam	O. Weigel, and E. Krueger,
33	2.53	Ca48Mg36Fe16	$n1.734 2V = 59 \gamma \land c46$	ante groundmass in ther-	Bo Ploi, Siam	0. Weigel, and E. Krueger,
34	2.92	$\mathrm{Ca_{49}Mg_{36}Fe_{15}}$	$\alpha 1.721 \beta 1.725 \gamma 1.746$	monzonitic tesche-	Marklowice, Poland	op. cu. W. Wawryk, (1935), M.A.,
35	1.77	$\mathrm{Ca_{45}Mg_{37}Fe_{18}}$	-	nue leucite-tephrite (?)	Vesuvius	0, 212 K. Muller, (1936), M.A., 6,
36	4.86	Ca49Mg37Fe14	$\alpha 1.701 \gamma 1.728 2V = 49$	monchiquite	Turja, Kola	E. H. Kranck, (1928), Fen-
37	1.53	Ca49Mg39Fe12	70-0431/1	analcime-basalt	The Basin, Colorado	W. Cross, (1897), Jour.
38	1.91	Ca46Mg44Fe10	ľ	analcime-basalt	Scano, Sardinia	H. S. Washington, (1914),
39	2.10	Ca44Mg44Fe12	α1.695 β1.706 γ1.720 2Vca60 γ∧c46	limburgite	Hopi Buttes, Arizona	Geol. Soc. Am., 47(1), 166,
40	2.18	Ca47Mg23Fe30	$\gamma \wedge c32-38$	ijolite	Ice River, Brit. Columbia	Analysis 15 J. A. Allen, (1914), Can.
41	2.34	Ca45Mg39Fe16	α1.703 β1.714 γ1.731	alkaline olivine-ba-	Old Pallas area, Co. Lim-	D. F. Ashby, (1946), Min-
42	1.59	Ca44Mg37Fe19	$\alpha 1.695 \beta 1.706 \gamma 1.726$	alkaline olivine-tra-	old Pallas area, Co. Lim-	oral. Mag., 21, 190 D. F. Ashby, op. cit.
43	4.33	Ca49Mg35Fe16	$\alpha 1.719 \beta 1.722 \gamma 1.742$	eny-pasant ''essexite-porphy-	erick, bure Stöffel, Westerwald	J. Holzner, (1934), Zeits.
44	4.50	$\mathrm{Ca}_{51}\mathrm{Mg}_{32}\mathrm{Fe}_{17}$	$\alpha 1.718 \beta 1.723 \gamma 1.738 \alpha 1.718 \beta 1.723 \gamma 1.738 \alpha 1.718 \beta 1.723 \gamma 1.738 \alpha 1.738 \beta 1.723 \gamma 1.738 \beta 1.728 \gamma 1.738 \gamma 1.$	ry nepheline-dolerite	Löbauer Berg	J. Holzner, op. cit.
45	5.50	Ca <sub>50</sub> Mg <sub>34</sub> Fe <sub>16</sub>	$\alpha 1.725 \ \beta 1.730 \ \gamma 1.750 \ 2V = 40$	nepheline-dolerite	Meiches, (Vogelsberg)	J. Holzner, <i>op. cit.</i>

TABLE 2—(continued)

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TABLE

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Garbh Eilean clinopyroxenes into the field of ferroaugite, mainly on an analysis of clinopyroxene ( $Ca_{41}Mg_{14}Fe_{4b}$ ) from an orthophyre vein in the Portrush sill, County Antrim. Of the many analyses studied, only one falls in the ferroaugite field, and then practically on the ferrosalite boundary (Fig. 3). The Portrush clinopyroxene should find no place in determining the trends of the present pyroxenes for the following reasons:

- 1. The origin of the orthophyre vein is related in part to reaction and rheomorphic injection. Consequently it is doubtful if the associated clinopyroxene is a "normal" type in that its precipitation occurred under strictly magmatic conditions.
- 2. It appears that the Portrush sill and its veins are the products of the consolidation of undersaturated tholeiitic magma (cf. Tilley, 1950, pp. 40-41). In his original account of the Portrush rocks, Harris (1937, pp. 102-104) recognized hypersthene (Of<sub>52</sub>) in addition to clinopyroxene. His descriptions include two clinopyroxene analyses, one of "enstatite-augite" (Ca<sub>42</sub>Mg<sub>44</sub>Fe<sub>14</sub>), the other poor in lime and approaching subcalcic augite (Ca<sub>25</sub>Mg<sub>41</sub>Fe<sub>34</sub>). The olivine-dolerites themselves carry normative hypersthene and are low in alkalies. The clinopyroxene in question plots very close to the trend of the Skaergaard clinopyroxenes from the ferrohortono-lite-ferrogabbros, a point commented on by Murray.

In tholeiitic magma rarely is fractionation so extreme that the composition of the clinopyroxene passes Wo29En30Fs41, i.e. the intersection of the course of clinopyroxene crystallization (after Hess, 1941) and the twopyroxene boundary (Poldervaart and Hess, 1951, p. 483; Fig. 5). Although only one common pyroxene occurs in alkali olivine-basalt magma, it is important to note that only two clinopyroxenes in Table 2 pass the two-pyroxene boundary in the direction of hedenbergite. Examples of clinopyroxenes of the diopside-hedenbergite series showing iron enrichment in excess of Ca45Mg25Fe30 must be rare in alkaline basic rocks. The retention of a large percentage of the available iron in the ferrous state in a reducing (relatively anhydrous) magmatic environment (Kennedy, 1948), and the continued crystallization of clinopyroxene after the disappearance of olivine under conditions of continual Fe/Mg enrichment would be fundamental conditions for such iron enrichment. Extreme fractionation of ijolitic types may furnish examples. However at compositions more iron-rich then approximately Ca44Mg36Fe20, continued fractionation of alkali olivine-basalt clinopyroxenes may result in progressive enrichment in the acmite molecule (Yagi, 1953), a trend often observed on a small scale in basic alkaline rocks as the zonal series, salite $\rightarrow$ aegirine-augite $\rightarrow$ aegirine, especially where the normal clinopyroxene (diopside or salite) abuts against a micro-crystalline alkaline residuum.

## The Contrasting Behavior of the Pyroxenes from Both Magma Types

The pyroxene assemblage in representatives of alkali olivine-basalt magma differs markedly from its equivalent in tholeiitic rocks in two important aspects, namely in the absence of orthopyroxene and pigeonite, and in the much more limited degree of clinopyroxene iron enrichment (Fig. 4), particularly in the replacement of  $Ca^{2+}$  by  $Fe^{2+}$ .

(i) In tholeiitic rocks, the frequently described mantling of olivine by orthopyroxene provides petrological testimony to the reaction relation between early-formed olivine and liquid (Bowen and Schairer, 1935).



Fig. 4. Clinopyroxene trends in basaltic magmas.

A - A' Alkali olivine-basalt clinopyroxene trend.

—→ Clinopyroxene course of crystallization in tholeiitic rocks (Poldervaart and Hess, 1951).

----> Clinopyroxene trend of the tholeiitic Skaergaard intrusion (Muir, 1951).

Although these authors consider the relation does not hold for certain "iron-rich basalts" which yield undersaturated differentiates, they regard the phenomenon as independent of the parental magma.

In the magma types under discussion, the presence or absence of orthopyroxene depends on the chemistry of the residual liquids formed during crystallization and subsequent fractionation. In many basic alkaline rocks (essexites, theralites, teschenites, lugarites), a microcrystalline mesostasis, often analcimic, consisting of alkali feldspar microlites, clinopyroxene and dusty iron ore, is frequently present, even in the early stages of magmatic evolution (Flett, 1910, p. 298; Browne, 1927, p. 375; Lehmann, 1930, Figs 3 and 4; Walker, 1930, p. 370; 1936, p. 280; Benson, 1942, p. 166). Such a mesostasis is widespread in the teschenites from all levels of the Black Jack sill (Table 3, Analysis 1). Under suitable condi-

				A COMPANY OF A	
	I	II	III	IV	v
SiO <sub>2</sub>	50.71	50.01	56.86	58.36	52.33
$TiO_2$	0.59	2.00	0.53	0.48	1.17
Al <sub>2</sub> O <sub>3</sub>	16.72	17.98	20.19	15.82	17.86
Fe <sub>2</sub> O <sub>3</sub>	3.26	3.05	3.63	4.87	3.12
FeO	5.49	3.26	1.40	2.53	3.89
MnO	0.01	0.10	0.13	0.27	0.08
MgO	0.42	3.13	0.33	0.59	3.61
CaO	3.27	7.09	1.64	1.99	1.88
Na <sub>2</sub> O	6.42	4.43	7.42	7.47	3.04
K <sub>2</sub> O	5.75	4.82	4.39	4.31	7.79
H <sub>0</sub> +	4.07	2.95	3.29	2.62	3.05
H <sub>0</sub> O-	0.49	0.27	0.07	0.72	1.02
PsO <sub>5</sub>	0.12	0.67	0.07	0.35	0.46
CO <sub>2</sub>	2.94	0.09		n.f.	0.26
etc.		0.12	-	0.04	0.21
Total	100.26	99.97	99.95	100.42	99.77
Norm.					
or	33.92	28.4	26.13	25.6	46.1
ab	33.01	20.4	47.67	49.8	23.8
ne	11.36	9.1	7.95	4.0	1.0
an		15.0	8.06		5.3
с			0.31		2.4
ac	÷			5.1	1 <u></u>
di	-	11.7		6.0	
hy				0.2	1999 - Carlos C.
ol	4.37	1.9	0.56		8.5
il	1.22	3.8	1.06	0.9	2.3
mt	4.87	4.4	3.25	4.6	4.4
hm		_	1.44	-	
ap	0.34	1.7		1.0	1.0
cc	5.50	-			
siderite	1.28	-			

TABLE 3. ANALYSES OF ANALCIME-SYENITES

Analysis I: Microcrystalline mesostasis, occurring as vein in teschenite, Black Jack sill, Gunnedah, New South Wales. Anal. J.F.G.W.

Analysis II: Analcime-syenite, forming felsic part of 80 foot sill, Utah. Anal. J. G. Fairchild (Gilluly, 1927, p. 205).

Analysis III: Analcime-syenite (1501), Morotu District, Sakhalin. Anal. K. Yagi (Yagi, 1953, Table 16).

Analysis IV: Segregation in analcime-syenite, Eilean Mhuire, Shiant Isles. Anal. E. G. Radley (Walker, 1930, p. 387).

Analysis V: Syenitic segregation (potash alkali-syenite) in upper teschenite of Lugar Sill boring, Mortonmuir, Cronberry, Ayrshire. Anal. G. A. Sergeant (Tyrrell, 1948, p. 165). tions, this type of residuum may crystallize as internal cross-cutting analcime-syenite (Table 3). The chemistry of this liquid prohibits any reaction relation involving olivine. In strong contrast the oversaturated nature of late-stage tholeiitic liquids is indicated by two analyses of tholeiitic residua (Walker, 1935; Vincent, 1950), containing 31–36 per cent normative quartz. Fractionation of alkali olivine-basalt magma does however occasionally yield syenitic products with normative quartz (Yagi, 1953, Table 16) and in certain instances, modal quartz (Raggart and Whitworth, 1932, p. 223). At just what stage this divergence to yield an acid alkali (pantelleritic) end product (Tilley, 1950, p. 43) occurs is not precisely known, but it is not believed to materially affect the pyroxene assemblage in relation to the non-appearance of orthopyroxene since olivine generally disappears before this stage is reached, and the ferromagnesian assemblage is dominated by sodic clinopyroxenes and alkaline amphiboles.

In both magma types, the nature of the olivine (where present) reflects the presence or non-appearance of orthopyroxene. The olivines in tholeiitic rocks are unzoned or rarely show slight zoning, indicating the readiness with which this mineral reacts with the magma, compared with the associated clinopyroxene or plagioclase which may be strongly zoned. Widespread normal zoning is a feature of the olivines of alkali olivinebasalt derivatives (Tomkeieff, 1939; Benson, 1942, p. 164; Johnston, 1953). The nature of the strongly fayalitic outer zones is analogous with the compositional relationships between the co-existing olivine and orthopyroxene in tholeiitic rocks, where the orthopyroxene may be the most iron-rich ferromagnesian silicate (Muir, 1951, p. 711; Ramberg and de Vore, 1951, Fig. 2). However as progressive iron enrichment occurs, the olivine may be the most iron-rich mineral (Muir, 1954, p. 382; Ramberg and de Vore,  $op \ cit$ .), a relationship in harmony with the experimental data of Bowen and Schairer (1935).

(ii) Edwards (1942), Walker and Poldervaart (1949) and Muir (1951) have correlated the observed crystallization trend in tholeiitic clinopyroxenes with atomic structure. The higher titania content of alkali olivine-basalt clinopyroxenes cannot be the reason for their relatively inert behavior, since during fractionation, tholeiitic titaniferous clinopyroxenes behave similarly to their titania-poor equivalents.

The following explanation of the two differing clinopyroxene trends is based mainly on petrological and mineralogical data, although physicochemical and crystal chemical reasoning may well be applied.

In tholeiitic magma, even in its early undersaturated stages, the reaction relation between olivine and liquid results in the continuous formation of "hypersthene molecules." While these are potential ortho-

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pyroxene or pigeonite, a variable percentage combines with highly diopsidic clinopyroxene (the "primitive" clinopyroxene of both magma types) to give augite, so that the modal pyroxene of tholeiites is greater than that of alkali olivine-basalts for the major part of their differentiation histories, even though in both cases a similar amount of lime is available for pyroxene formation.

Relevant data on medium grained differentiated intrusions (where more reliance can be placed on micrometric data) is set out in Table 4. These intrusions possess compositions representative of their parental magma types (see Walker, 1940, Table 3; Walker and Poldervaart, 1949, Table 24; Nockolds and Allen, 1954, Table 17). Pegmatitic facies or rocks with appreciable amphibole or mica are not included in the tabulation. The tholeiitic types possess a higher modal pyroxene content, averaging 30-45 per cent (see Turner and Verhoogen, 1951, p. 183), compared with alkali olivine-basalt rocks where the modal pyroxene varies from 18-24 per cent (see also Walker, 1934, Table 1). There is no notable divergence in the CaO content of both series, each carrying 50-60 per cent of modal plagioclase of similar basicity.

The principal pyroxene relationships visualized are as follows:

olivine+SiO<sub>2</sub>→orthopyroxene orthopyroxene+diopside→augite olivine+SiO<sub>2</sub>+diopside→augite (tholeiite) In silica-deficient basic rocks-SiO<sub>2</sub>→olivine+diopside (alkali olivine-basalt)

Thus in the early magmatic stages, the tholeiitic clinopyroxene (augite) shows replacement of  $Ca^{2+}$  by  $Fe^{2+}$ , compared with the diopsidic type in alkali olivine-basalt at an equivalent stage. In its subsequent differentiation, tholeiitic magma may involve nearly double the amount of clinopyroxene in alkali magma.

While fractionation results in enrichment in iron relative to magnesium (and in certain instances, absolute iron enrichment), the response of the principal ferromagnesian mineral series to this enrichment varies in each magma type. In tholeiitic rocks, most of the Fe/Mg enrichment occurs in the olivine (if it still persists), orthopyroxene or pigeonite; the clinopyroxene lags behind these minerals. While falling temperature favors clinopyroxene iron enrichment, the additional and more difficult replacement of Ca<sup>2+</sup> by Fe<sup>2+</sup> is induced by the limited amount of available magmatic lime. Exceptions to the relatively high pyroxene content of tholeiites may be noted. The Skaergaard marginal gabbros, considered to represent the parental magma, contain 23 per cent pyroxene, a figure which increases to 41 per cent in the middle gabbros (Wager and Deer, 1939, p. 95 and p. 144). With this increase in pyroxene, which now reveals appreciable replacement of Ca<sup>2+</sup> by Fe<sup>2+</sup> (Fig. 4), the modal olivine de-

Name of intrusion	Range of CaO (weight per cent)	MgO	FeO	Modal olivine (volume per cent)	<sup>a</sup> Modal pyroxene	Modal plagioclase	Reference
Black Jack sill, Gunnedah, N. S. W.	10.25-8.12	9.57-2.97	9,57-7.93	23.0-0.0 (based on 6	16.4-29.2 0 modes)	52.2 to average around 45	Wellow (1020)
Loch Mealt-Kilt Rock sill,	11.61-11.47	5.98-5.32	7.40-5.77	17.1-4.6	14.3-25.2	73.7-58.8	Walker (1932)
Trotternish, Skye No. 6 Bore, Mt. Nebo sill,	10.7 - 8.29	10.8 - 9.02	9.95-6.3	18.5-12.0	12.0-22.6	not determined	Edwards (1953)
N. S. W. Circular Head laccolith, Tasmania	9.95-8.20	11.84-5.24	10,94-6.41	24.9-4.4	13.1-27.3	76.6-49.4 (in- cludes zeolite	Edwards (1941)
George Washington Bridge section, Palisades sill,	10.65-8.38	17.48-3.47	11.54-7.70	22.0-0.0	51.8-29.4	and mesostasis) 65.8-32.6	Walker (1940)
N. J.* Dillsburg sill, Penn.* Whin sill (generalized fig-	$\begin{array}{c} 10.18 - 8.85 \\ 9.46 - 8.21 \end{array}$	7.3 - 4.33 5.90 - 4.42	9.19-7.85 11.44-8.95	2.0- 0.0	57.5-37.4 38.7-31.6	43.7 - 30.0 52.3 - 49.0	Hotz (1953) Holmes and Harwood (1928)
ures) <sup>+</sup> Hangnest sill, South Afri- ca <sup>*</sup>	9.40-8.89	7.32-5.14	9.12-8.85	]	50.2-40.6 (average	49.8-40.7 (average 40.7)	Walker and Poldervaart, (1941)
Elephant's Head dyke and New Amalfi sheet, Ma- tatiele, South Africa*	13.86-8.4	9.77-4.76	11, 18–8, 74	12.3-0.0	$^{42.9}_{\pm 0.4-37.2}_{\rightarrow (26.5)}$	45.5-40.5 $\rightarrow (33.4)$	Poldervaart (1944)

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creases. Tholeiites may retain their initial moderately low pyroxene content (when no great degree of iron enrichment would be anticipated), if reaction is prevented by the residual liquids diffusing through the crystal interstices. However olivine frequently disappears at a relatively early stage in tholeiitic evolution, and indeed this mineral may be antipathetic with orthopyroxene (Walker and Poldervaart, 1941*a*, p. 143). In the later stages of pyroxene fractionation when re-entry of Ca<sup>2+</sup> occurs (Edwards, 1942), and the replacement is dominantly Fe<sup>2+</sup> for Mg<sup>2+</sup>, the additional withdrawal of lime is reflected in a decrease in modal pyroxene, despite albite enrichment in the plagioclase e. g. decrease in modal pyroxene occurs at this stage in the Palisades, Hangnest and Dillsburg sills. Possibly the two-pyroxene boundary is reached about this stage and the main Fe/Mg enrichment now occurs in the clinopyroxene.

In alkali olivine-basalt magma, the ferromagnesian assemblage consists of diopsidic clinopyroxene and olivine. In the initial stages, the early separation of forsteritic olivine greatly increases the normative Wo content of the magma (Kennedy, 1933, p. 252). In the absence of possible localized crystal accumulation, the failure of the reaction relation results in a moderately low near-constant amount of clinopyroxene. With decreasing temperature, the bulk of Fe/Mg enrichment is borne by an everdiminishing quantity of olivine, which becomes more fayalitic (and in many instances, more strongly zoned). Exsolution lamellae are uncommon in alkali olivine-basalt clinopyroxenes. The absence of the reaction relation limits the amount of En-Fs in solid solution (cf. Poldervaart and Hess, 1951, p. 488). In these clinopyroxenes, the lack of alteration in the presence of residual magmatic solutions (except in dykes of "white trap"), (Flett, 1931, p. 47; 1932, p. 145; Browne, 1924, p. 244; Raggatt and Whitworth, 1932, p. 217; Campbell, Day and Stenhouse, 1932, p. 352) may well be consequent on the greater structural stability resulting from more limited replacement of Ca<sup>2+</sup> by Fe<sup>2+</sup>, compared with their tholeiitic equivalents (see also Harry, 1954, p. 85).

### ACKNOWLEDGMENTS

The bulk of this study was carried out in the Department of Mineralogy and Petrology, Cambridge, during the writer's tenure of a Royal Dutch/Shell Commonwealth Post-Graduate Scholarship. This financial assistance is gratefully acknowledged.

The writer expresses his thanks to Professor C. E. Tilley and Dr. S. R. Nockolds for helpful discussions on pyroxene problems, and to Professor H. H. Hess and Dr. G. M. Brown for critically reading the manuscript. Dr. S. O. Agrell gave permission to quote the analysis of the Camphouse titaniferous clinopyroxene, carried out by Mr. J. H. Scoon.

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Manuscript received Dec. 23, 1955.