# OPTICAL AND CHEMICAL STUDIES OF PYROXENES IN A DIFFERENTIATED TASMANIAN DOLERITE

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## Abstract

At Red Hill in southern Tasmania a large near vertical dike-like intrusion of tholeiitic dolerite, one mile in width and about five miles in length crops out. In this body marked differentiation has given rise to a series of rocks varying continuously from undifferentiated dolerite to granophyre; the latter occurring in the highest parts of the intrusion. Five pyroxenes, separated from rocks representative of the differentiation series, have been chemically analyzed and the optical properties determined. These pyroxenes are a coexisting pigeonite and augite, two ferroaugites and a ferrohedenbergite. To outline the complete fractionation series a number of other pyroxenes have been determined optically. Orthopyroxene occurs as a primary phase in a zone approximately fifty feet wide in dolerites adjacent to, and including, the chilled contacts of the intrusion, but elsewhere pigeonite is the only Ca-poor pyroxene present. Pigeonite also has crystallized in the dolerites adjacent to the contacts, where it has, in some cases, partially inverted to orthopyroxene. A member of the augite series crystallizes in cotectic equilibrium with the pigeonite and during fractionation both pyroxenes become progressively enriched in Fe, primarily at the expense of Mg. At the limit of the two-pyroxene field pigeonite ceases to form but the Ca-rich pyroxene continues to crystallize, steadily increasing in Fe content with fractionation, ultimately to attain the composition of ferrohedenbergite in the more acid granophyres. The trend of crystallization with fractionation closely parallels that from the Skaergaard intrusion. Exsolution phenomenon occur in both series of pyroxenes throughout much of the sequence, but is virtually absent in the ferrohedenbergite, probably owing to the relatively low temperature of crystallization.

# INTRODUCTION

During the last two decades considerable attention has been paid to the composition and course of crystallization of pyroxenes from basaltic magmas. The general trend of crystallization of pyroxenes during fractionation was outlined independently by Hess (1941) and Edwards (1942), who showed that normally two series of pyroxenes crystallize through the greater part of the cooling history of basic magma. They also recognized the relation between orthopyroxene and pigeonite and explained the significance of some of the exsolution textures. Hess (1941) noted that in the late fractionation stages only a single pyroxene phase crystallizes and suggested that this behavior might be accounted for by a solid solution with a minimum forming in the pyroxene system at the limit of the two-pyroxene field.

Poldervaart and Hess (1951) clearly summarized the relations between the different pyroxenes found in basaltic magmas and treated the exsolution textures in detail. To explain the cessation of crystallization of pigeonite at the limit of the two-pyroxene field, in addition to the hypothesis already suggested by Hess (1941), they proposed the alter-

native that Ca-poor pyroxene may react with the liquid to form fayalite olivine. The problem was again considered by Muir (1954) who outlined a further explanation of this behavior. Edwards (1942, p. 602) suggested that rapid crystallization at high temperature could result in complete miscibility in the pyroxene system, and Kuno (1955) has since shown that under certain conditions, probably rapid cooling, the immiscibility gap between the Ca-rich and Ca-poor series of pyroxenes does not in fact exist.

The Skaergaard intrusion of East Greenland is the only example in the literature from which adequate data is available on the behavior of pyroxenes with strong fractionation of basaltic magma. Following on the original investigation by Wager and Deer (1939), Muir (1951) and Brown (1957) have carried out detailed studies of the pyroxene phases, establishing the trend of crystallization. Brown also gives a comprehensive account of the exsolution and inversion phenomena.

Edwards (1942) in a broad study of the differentiation of the Tasmanian dolerites has considered the relations between the different pyroxenes in some detail, and explained the occurrence of the two separate series of pyroxenes on the basis of their atomic structure. The present paper records the results of a detailed chemical and optical investigation of the pyroxene phases occurring in the large Red Hill intrusion of Tasmania, in which an acid granophyre occurs; the differentiation thus being more marked than in any intrusion studied by Edwards. In the early and middle stages of fractionation of the magma of the Red Hill intrusion, and of the Tasmanian dolerites as a whole, representatives of the two main series have crystallized in cotectic equilibrium. In the late stages of fractionation, as exemplified in the Red Hill intrusion, a single pyroxene phase of the Ca-rich series has crystallized. The range in composition of the pyroxenes and their trend of crystallization with fractionation is closely comparable to that found in the Skaergaard Intrusion.

# THE TASMANIAN DOLERITES

The Tasmanian dolerites were intruded into an essentially flat-lying sequence of Permian and Triassic sediments as sheets, commonly exceeding 1,000 feet in thickness, and as irregular transgressive bodies, and large dike-like intrusions up to one mile in width. The dolerite, generally considered to be of Jurassic age (Banks, 1958, p. 234), crops out over an area exceeding 6,000 square miles, and originally probably extended over more than twice this area. Edwards (1942) has shown that the undifferentiated magma is of remarkably uniform composition throughout Tasmania, and recent work by the writer completely confirms this finding. The dolerite magma belongs to the tholeiitic basalt association and it is closely allied in composition to the dolerites of the Karroo, the Palisadan province, the British Guiana and Brazilian dolerites and especially to those of Antarctica.

Edwards (1942) in his excellent chemical study of the Tasmanian dolerites outlined the differentiation trend and found that in the lower parts of the sheet-like intrusions rocks markedly enriched in magnesia occur, followed upwards by dolerites progressively enriched in iron relative to magnesia, with moderate absolute iron enrichment, and en-



FIG. 1. Triangular diagram showing the differentiation trend in the Red Hill intrusion. The Skaergaard trend is included for comparison.

richment in alkalies and silica. In the Red Hill intrusion the differentiation has been more extreme and the latest products are granophyres, markedly enriched in iron, silica and alkalies and impoverished in magnesia and lime. The differentiation trend is illustrated in Fig. 1, where it is compared with that of Skaergaard. A detailed account of the field occurrence and petrology of the Red Hill intrusion will be presented elsewhere, and only a short summary of these is given here.

## FIELD RELATIONS

The Red Hill intrusion is situated some 20 miles to the southwest of Hobart in southern Tasmania, and approximately 10 miles south of the Mount Wellington sheet, which Edwards (1942) has studied. The in-

trusion crops out as a large vertical dike-like body one mile in width, and can be traced in a north-south direction for over five miles. The structural interpretation indicates that this dike-like intrusion extends upwards for over 1,000 feet from the roof of an underlying dolerite sheet of approximately 1,300 feet in thickness (Fig. 2). The field evidence conclusively shows that this dike-like intrusion made room for itself by lifting the sediments in a similar manner to that in which the sheets were emplaced. The dike therefore possessed a roof of sediments, which have subsequently been removed by erosion.

Owing to the hilly topography in the Red Hill area a section of the intrusion 1,000 feet in height is available for study as well as an excellent



FIG. 2. Diagrammatic block diagram of the Red Hill intrusion.

river section at right angles to the trend of the dike. Because only the upper part of the dike-like intrusion is exposed, all the rocks revealed are more acid than the undifferentiated magma, as represented by the chilled contacts. However above the floor of the underlying dolerite sheet, out of which the Red Hill dike arose, more basic accumulative rocks must occur, comparable in composition to those of the magnesia-rich zone in the lower parts of the sheets, described by Edwards.

In the lowest exposed parts of the Red Hill intrusion the chilled dolerites adjacent to the intruded sediments pass gradationally into coarser varieties which become progressively more acid as the center of the dike is approached in a horizontal traverse. Here the rock is a medium grained dolerite which passes vertically upwards, by complete gradation, into increasingly more acid rocks and finally into granophyre towards the summit of Red Hill. This change in composition takes place over a vertical height of the order of 600 to 800 feet and is brought about essentially by a steady increase in the quartz and potash feldspar at the expense of pyroxene and plagioclase; these latter two minerals changing progressively in composition throughout the sequence.

The petrological, mineralogical and field data conclusively show that the dolerite-granophyre association in the Red Hill intrusion has been produced by a process of differentiation of the dolerite magma by means of fractional crystallization and the gravitational movement of phases.



FIG. 3. Typical normal quartz dolerite (specimen M210) consisting of pigeonite and augite (dark, high relief) molded on plagioclase laths (colorless), with a large opaque crystal of iron ore. Scale mark is 1 mm. in length.

## SUMMARY OF THE PETROGRAPHY

Invariably at the contacts with the sediments the dolerite is chilled to a glassy or very fine grained rock containing a few per cent of microphenocrysts. These are predominantly of euhedral orthopyroxene, although in some cases small augite and plagioclase microphenocrysts also occur. When crystalline the groundmass consists of minute granules of pyroxene and small laths of plagioclase (An<sub>65</sub>). The groundmass pyroxene in such cases appears to consist of augite and orthopyroxene.

Away from the contacts the dolerite increases rapidly in grain size. The bulk of the dolerite is medium grained and consists essentially of pyroxene, plagioclase ( $An_{60}-An_{70}$ ), an intersertal mesostasis composed of

quartz and potash feldspar, usually in micrographic intergrowth, with iron ore as an important accessory. The pyroxene is strongly molded on plagioclase laths to give a subophitic texture (Fig. 3).

In a zone extending up to 200 feet from the chilled vertical contacts of the Red Hill intrusion three varieties of pyroxene occur in the dolerite: orthopyroxene, pigeonite and augite. The primary orthopyroxene increases in grain size to about 1 mm. as compared with about 0.3 mm. in the chilled contacts. It generally builds prismatic crystals, which, however, are rarely euhedral owing to interference by plagioclase laths. The primary orthopyroxene persists for about 50 feet from the chilled contacts and is not found elsewhere in the exposed part of the intrusion. It is commonly mantled by pigeonite.

Within a few feet of the chilled margins of the Red Hill intrusion the groundmass pyroxene can definitely be identified as pigeonite and augite in approximately equal proportions. Both increase rapidly in grain size and within 100 feet of the contact attain an average size of about 1 mm. The two pyroxenes are indistinguishable in thin section except by the optic angle. Both are usually anhedral, rarely subhedral, but commonly somewhat elongate, and include plagioclase laths subophitically. Some of the pigeonite grains in a zone up to 200 feet from the contacts have partially or completely inverted to orthopyroxene, which contains exsolution lamellae, probably of augitic composition (Poldervaart and Hess, 1951).

Apart from the zone immediately adjacent to the contacts, the pyroxene of the quartz dolerites consists of pigeonite and augite only. Generally they are present in about equal proportions, except in the more acid dolerites, transitional to granophyre, when the pigeonite decreases in amount. The proportion of pyroxene in the quartz dolerites ranges from about 35% to less than 15% by volume; the highest concentration occurring in the dolerites adjacent to the chilled contacts, and the lowest proportion in the more acid dolerites in the central and higher parts of the intrusion, below the granophyre. The two clinopyroxenes, anhedral to subhedral in form and molded strongly on plagioclase laths, average between 1 and 2 mm. in size, and usually occur as individual crystals surrounded by areas of rather finer grained plagioclase and mesostasis. However in some cases several grains of pyroxene have crystallized in close proximity to one another to form large irregular plates up to 5 mm. across. Not uncommonly the pigeonite and augite are intergrown with one another, each having the same crystallographic orientation.

The quartz dolerite in the central parts of the dike passes upwards gradationally into fayalite granophyre essentially by a progressive increase in the proportion of quartz and potash feldspar at the expense of

## PYROXENES IN A TASMANIAN DOLERITE

pyroxene and plagioclase. A fayalitic olivine (Fa<sub>90</sub>) makes its appearance at this level and coincides with a marked decrease and final disappearance of pigeonite. The pyroxene of the augite series, a ferroaugite, continues to crystallize. The fayalite granophyres have a texture very similar to that of the quartz dolerites, except that the pyroxene is much smaller in amount, usually less than 10% by volume. The pyroxene is strongly molded on plagioclase laths (Fig. 4). The plagioclase constitutes some 40% to 50% by volume of the fayalite granophyre and has a



FIG. 4. Ferroaugite of fayalite granophyre strongly molded on colorless plagioclase laths. Scale mark is 1 mm. in length.

composition about An<sub>60</sub>. The quartz and potash feldspar, forming 30% to 50% of the rock, occurs in well developed granophyric intergrowths or in some cases as anhedral grains. Iron ore is present as a major accessory and usually to the extent of about 2% by volume.

The granophyre, into which the fayalite granophyre passes upwards gradationally by a further increase in the proportion of quartz and alkali feldspar, contains only a single ferromagnesian phase, a ferrohedenbergite, the fayalitic olivine having ceased to crystallize. The granophyre consists essentially of ferrohedenbergite (5% to 9% by volume), plagioclase (An<sub>50</sub>-An<sub>15</sub>) present to the extent of 15% to 30%, very abundant quartz and potash feldspar (50% to 70%), which is usually intergrown to give the rock the typical granophyric texture, and a variable amount of iron ore. The pyroxene has a distinctly different habit from that in the quartz dolerites and fayalite granophyres, since it occurs as independent elongate crystals, which, however, rarely exhibit crystal faces, owing to strong interference by other minerals (Fig. 5). In some thin sections seemingly unconnected fragments of pyroxene, all of the same orientation, may extend over a distance in excess of 10 mm.



FIG. 5. Elongate but irregularly shaped ferrohedenbergite in granophyre from Red Hill. Iron ore granules are associated with the pyroxene. The light areas consist of quartz and alkali feldspar in granophyric intergrowth and also plagioclase laths. Scale mark is 1 mm. in length.

# METHODS OF DETERMINATION OF OPTICAL PROPERTIES

The methods employed in the determination of the optical properties of the pyroxenes were essentially those of Hess (1949). Refractive indices were determined by the usual immersion methods on the crushed pyroxene fraction. The index being measured was bracketed between liquids 0.005 apart, and the final determination, carried out under sodium light, was by mixing the liquids until the index was exactly matched. The index of the liquid was then measured with an Abbe refractometer. The  $\beta$  index of clinopyroxenes with optic plane ||(010)| was measured on (100) parting tablets (Hess, 1949, p. 627), and  $\alpha$  and  $\gamma$  were determined by the minimum and maximum index found in the crushed sample. This method for  $\alpha$  and  $\gamma$  is not as accurate as determination of them by calculation, from the birefringence, since the pyroxene is generally slightly zoned. Hence the birefringence, derived from the refractive indices, tends to be a little high. The determination of the indices of pigeonites was carried out on grains whose orientation was checked, in each case, by observing the interference figure (Hess, 1949, p. 628). When it was not possible to separate the clinopyroxene from the rock, crystals with an optic axis vertical were dug out of a slide and the  $\beta$  index measured. The composition of the pyroxene was then determined from the  $\beta$  index and the 2V, by referring to the graph of Hess (1949, p. 634). The orthopyroxenes from the chilled marginal zones of the intrusion, were determined from measurements of  $\alpha$  and  $\gamma$  on a separated sample of the pyroxene, and referring to the graph of Poldervaart (1950, p. 1076). Measurements of the optic angle were also used as an independent check. The accuracy of the refractive index determinations is considered to be better than  $\pm 0.001$ .

The optic angle of each of the pyroxenes was determined on a universal stage, using the conoscopic method of orientation, by direct rotation from optic axis to optic axis in sodium light. After applying the appropriate index corrections the accuracy of the determinations is better than  $\pm 1^{\circ}$ .

## CHEMICAL ANALYSES OF THE PYROXENES

Five chemical analyses have been made of pyroxenes from four of the main rock types of the Red Hill intrusion (Table 1). The analyses were carried out, in most cases, on pure material, separated by using the isodynamic magnetic separator in conjunction with heavy liquids. It was found impossible to completely eliminate the augite from the pigeonite of the quartz dolerite (M210); a correction was made to the analysis for 10% augite impurity, and then recalculated to 100%. The alkalies were determined by flame photometer and the total iron colorimetrically, but the remainder of the analysis was carried out by classical methods.

The generalized formulae for clinopyroxene, after Berman (1937), Hess (1949) and Kuno (1955) is:

$$W_{1-p}(X, Y)_{1+p}Z_2O_6$$

where

$$W = Ca^{2}, Na^{1}, K^{1}$$
  

$$X = Mg^{2}, Fe^{2}, Mn^{2}, Ni^{2}$$
  

$$Y = Al^{3}, Fe^{3}, Cr^{3}, Ti^{4}$$
  

$$Z = Si^{4}, Al^{3}, Ti^{4}, Fe^{3}$$

The analyses (Table 1) have been recalculated on the basis of six oxygen atoms (Table 2), using the method outlined by Hess (1949, p. 625), in

	3	ЗА	**	ŵ	9
SiO <sub>2</sub> Al <sub>8</sub> O3	51.32	48.31 0.53	49.63	48.00 1 17	46.59
Fe203	0.87	1.35	1.53	1.20	1.82
FeO	14.71	31.33	20.94	26.65	28.93
MnO	0.30	0.62	0.47	0.53	0.53
MgO	13.64	10.13	9.08	4.71	1.04
Nac	06.01	0.08	14.4/	10.50	18.08
K 0	0 13	0.10	07-0	0.18	0.25
TiO <sub>2</sub>	0.42	0.58	0.67	0 75	1.50
$H_2O$	0.44	0.80	0.28	0.30	0.31
	99.59	100.00	99.62	100.11	100.17
$\stackrel{NX}{\sum}_{2V_x}^{NX}$	1.692 1.697 AV: 47°	1.707 1.708 1.708 0, 0, 0, 10, 10	1.710 1.717 Av. 414°	1.721 1.727a 1.751 Av. 50°	$\begin{array}{ccc} Purple & Green \\ 1.736 & 1.735 \\ 1.744 & 1.742 \\ 1.765 & 1.764 \\ \Lambda_{V}, 54^{\alpha} & \Lambda_{V}, 57_{2}^{\alpha} \end{array}$
	45, 40, 404, 474, 484 484	13, 17, 21; 90 opt. plane ]r 1 (010)	40, 41, 41 <sup>1</sup> / <sub>2</sub> , 41 <sup>1</sup> / <sub>2</sub> , 42 <sup>1</sup> / <sub>2</sub> ,	$46-53\frac{1}{2}, 48\frac{1}{2}, 49\frac{1}{2}, 49\frac{1}{2}, 50\frac{1}{2}, 51\frac{1}{2}, 51\frac{1}$	51.3/4, 524, 564, 564, 564, 57, 61, 53.3, 544, 58.1/4
		$ \begin{array}{c} 11\frac{1}{2}, 13, 19, \\ 25, \text{ opt.} \\ 11 (010), \\ 11 (010), \\ 11 \end{array} $	Ľ.	Rims about 7° higher than cores.	$ \begin{array}{l} {} {} {} {} {} {} {} {} {} {} {} {} {}$
Exsolution lamellae	(001)	(001)	(001)	(001)	None
Atom % Ca Mg Fe*	33.8 40.1 26.1	10.8 43.4 45.8	31.4 30.0 38.6	36.6 14.5 48.9	41,4 3.3 55,3
* Fe=Fe <sup>2</sup> +Fe <sup>n+</sup> +A	Mn,				

Samples:

Augite from quarts dolerite M210; centre of Red Hill Dike, Snug River.
 A. Piconoufe from quarts dolerite M210, Analysis corrected for 10% augits impurity (3) and recalculated to 100%.
 Ferroaugite from quarts dolerite M305, centre of Red Hill Dike on the northern flank of O'Birn's Hill, 465 feet above Snug River.
 Ferroaugite from favalite granophyre M12; northern flank of Red Hill Dike on the northern flank of O'Birn's Hill, 465 feet above Snug River.
 Ferroaugite from granch of Reid M12; northern flank of Red Hill at road level (altitude 715 feet) and about 550 yards from western contact of the Red Hill Dike, Analyses by lam AcDougila

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	3	3A	4	5	6
Si	1.957	1.953	1.947	1,939	1.926
ZAI	0.048	0.024	0.063	0.058	0.047
Ti		0.019	0.002	0.004	0.036
Al	0.021	-		-	-
Fe <sup>3+</sup>	0.028	0.041	0.047	0.039	0.055
Fe <sup>2+</sup>	0.468	1.058	0.686	0.900	1.002
Mn	0.009	0.019	0.017	0.017	0.017
WXY Mg	0.775	0,609	0.581	0.284	0.065
Ca	0.653	0.264	0.610	0.716	0.803
Na	0.018	0.012	0.014	0.015	0.020
K	0.005	0.005	0.005	0.005	0.010
Ti	0.012	-	0.019	0,020	0.011
Z	2.005	1.996	2.012	2.001	2.009
WXY	1,989	2.008	1.979	1.996	1.983
% Al in Z	2.4	1.2	3.1	2.9	2.3
% Ti in Z	(1-1-1-1)	0.8	0.1	0.2	1.8

TABLE 2. ANALYSES OF TABLE 1, RECALCULATED ON THE BASIS OF SIX O ATOMS

which the electrical charges are always balanced between the several groups. According to Hess in a completely satisfactory analysis the number of cations to six oxygen atoms in the WXY and Z groups is  $2.00 \pm 0.02$ ; all the analyses carried out on the Red Hill pyroxenes meet this requirement.

In the recalculation of four of the five analyses it has been necessary to include all the Al<sup>3</sup> in the Z group, and even then there is still a deficiency in charge, which must be made up by assuming that some Ti<sup>4</sup> and/or Fe<sup>3</sup> is also present in the tetrahedral position. It has usually been tacitly assumed that Ti<sup>4</sup> will enter the tetrahedral position preferentially (Hess, 1949; Muir, 1951), but, as pointed out by Kuno (1955) and Brown (1957), it is possible that Fe<sup>3</sup> may also occur in this position in the pyroxenes. The ionic radii for sixfold coordination are (Ahrens, 1952);

The Fe<sup>3</sup> ion is slightly smaller than Ti<sup>4</sup> and therefore may replace Si<sup>4</sup> more readily, but since Ti<sup>4</sup> is quadrivalent this ion may be preferentially included in this position. That Fe<sup>3</sup> can enter the tetrahedral position in silicates, and particularly in alkali feldspars, has been well demonstrated by Faust (1936), Rosenqvist (1951), and Coombs (1954). Kuno (1955)

shows that Fe<sup>3</sup> may also be present in the Z group in clinopyroxenes. Thus although the recalculation of the analyses of the Red Hill pyroxenes is made by assuming the Ti<sup>4</sup> preferentially enters into the tetrahedral position, this does not exclude the possibility that some Fe<sup>3</sup> occurs in this position.

# The Variation in Composition of the Pyroxenes with Fractionation

Enrichment in Fe at the expense of Mg is the major variation in the composition of the pyroxenes during fractionation of the Red Hill magma, and this is accompanied by smaller variations in Ca (Fig. 6).



ATOMIC %

FIG. 6. Crystallization trend of the pyroxenes from the Red Hill intrusion. Tie lines join coexisting pyroxene phases. 1, 2A, 2B, orthopyroxene; 2C, 3A, 4A, pigeonite; 2, 3, augite; 4, 5, ferroaugite; 6, ferrohedenbergite.

These trends will be discussed below but reference will first be made to those cations which enter into the pyroxene lattice in small amount.

The Al content of the Red Hill pyroxenes is lower than in many analyzed clinopyroxenes (Hess, 1949; Muir, 1951; Kuno, 1955; Brown, 1957). As Brown (1957) found in the Skaergaard clinopyroxenes it decreases steadily with fractionation, and the amount of Al entering into the augite is somewhat higher than in the coexisting pigeonite.

With fractionation the Ti content of the clinopyroxene increases progressively, by contrast to Skaergaard, where there is but little change in Ti (Muir, 1951; Brown, 1957). Also Ti is present in greater amount in the pigeonite than in the associated augite; the reverse of the behavior in Skaergaard (Brown, 1957).

The Mn content of the pyroxenes from the Red Hill intrusion increases with the  $Fe^2$  content; this being a consequence of the similarity in charge, electronegativity and ionic radius of the two ions (Wager and

	1	1A	2	2A
$lpha egin{array}{c} lpha \ eta \ \gamma \end{array}$	1.675 1.687	1.675	1.788	
2V	Av. 84°(-) 82 <sup>1</sup> / <sub>2</sub> , 83, 84, 86, 86 <sup>1</sup> / <sub>2</sub> rim av. 62 <sup>1</sup> / <sub>2</sub> (-)	Av. 84°(-) 80 <sup>1</sup> / <sub>2</sub> , 82, 82, 84, 84, 85, 85 <sup>1</sup> / <sub>2</sub> , 86 rim av. 62°	Av. 47°(+) 46 <sup>1</sup> / <sub>2</sub> , 47, 47, 47, 47, 47 <sup>1</sup> / <sub>2</sub> , 48 core av. 7° higher than rim	Av. 69°(-) 62, 64, 66, 68, 68, 68, 74, 81.
Composition	Of <sub>15</sub>	Of <sub>15</sub>	${{ m Ca}_{{39},5}}{ m Mg}_{{45}}$ Fe <sub>15,5</sub>	Of <sub>24</sub>
	2B	2C	4A	
β		1.685	1.719	1.5
2V	58°(-)	Av. 18°(+) 17, 19. Opt. plane ⊥ (010)	Av. $12\frac{1}{2}^{\circ}(+)12$ , 12, 14. Opt. plane $  (010) $	
Composition	Of <sub>33</sub>	Ca <sub>7.5</sub> Mg <sub>63</sub> Fe <sub>29.5</sub>	$\begin{array}{c} Ca_{13}Mg_{3!,5} \\ Fe_{55,5} \end{array}$	

## TABLE 3. OPTICAL PROPERTIES OF PYROXENES

1. Microphenocrysts of orthopyroxene in chilled dolerite M172; eastern contact of Red Hill dike

1A. Microphenocrysts of orthopyroxene in chilled dolerite M200; upper contact of northern sill, northeast of Longley.

2. Augite of M212; medium grained quartz dolerite about 40 feet from western contact of the Red Hill dike in Snug River.

- 2A. Primary orthopyroxene from quartz dolerite M212.
- 2B. Most iron-rich primary orthopyroxene from M212.
- 2C. Pigeonite from quartz dolerite M212.
- 4A. Pigeonite from M395.

Mitchell, 1951; Ringwood, 1955). Again, as expected, the Mn content of the pigeonite is considerably greater than that of the coexisting augite, because of the relatively higher Fe content of the pigeonite.

The amount of  $Fe^3$  increases slightly with fractionation, and the pigeonite is relatively enriched in this constituent as compared with augite, the opposite to Brown's (1957, p. 518) findings in the pyroxenes of the Skaergaard intrusion.

The alkali content of the Red Hill pyroxenes remains uniformly low; there is no significant variation with fractionation.

In Fig. 6, together with the analyzed pyroxenes from Red Hill, are

plotted a number of pyroxenes whose compositions were estimated from optical data (Table 3).

At the chilled margins of the Red Hill dike, and indeed in the contacts of all the Tasmanian dolerites, small euhedral microphenocrysts of Mgrich orthopyroxene (Of<sub>15</sub>) occur embedded in either a glassy base or more commonly in a very fine-grained holocrystalline groundmass. It is apparent that this pyroxene began to crystallize some little time before emplacement of the dolerite magma. When crystallization began the magma was below the clinopyroxene-orthopyroxene inversion curve (Fig. 7), in the orthopyroxene stability field. The orthopyroxene is usu-



Fig. 7. Suggested temperature of crystallization of basaltic magma, and its relation to the orthopyroxene-clinopyroxene inversion curve (after Hess, 1941).

ally uniform in composition but commonly has a very thin rim which may be as iron-rich as Of<sub>29</sub>.

Pyroxene in the groundmass of the contact rocks occurs as minute granules and appears to consist of both augite and orthopyroxene. However within a few feet of the contact pigeonite takes the place of orthopyroxene, so that the magma has crossed the inversion curve into the clinopyroxene stability field.

Primary orthopyroxene, mainly as phenocrysts, persists for about 50 feet from the chilled contacts of the Red Hill dike, after which pigeonite is the only Ca-poor primary pyroxene crystallizing. Dolerites from this marginal zone usually contain four different pyroxenes; primary orthopyroxene, orthopyroxene resulting from the inversion of pigeonite, pigeonite and augite. Therefore, because of the difficulty of separation,

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it was necessary to determine these pyroxenes optically (Table 3). The primary orthopyroxene ranges in composition from Of<sub>16</sub> to Of<sub>33</sub> although zoning is not strongly developed. Pyroxene (2A) (Fig. 6) is the average of eight determinations and pyroxene (2B) is the most Fe-rich primary orthopyroxene determined. The assumption is made in plotting that the primary orthopyroxene contains the normal 3.5% Ca (Poldervaart and Hess, 1951). The orthopyroxene occurs as anhedral to prismatic crystals which may reach 2 mm. in size, and is commonly mantled by pigeonite which has, in some cases, subsequently inverted to orthopyroxene. Specimen (M212) contains about 40% pyroxene, but less than 1% of this is primary orthopyroxene.

Pyroxenes (2) and (2C) in Fig. 6 are the augite and pigeonite respectively, which together make up the bulk of the pyroxene in specimen (M212). The clinopyroxenes are anhedral to subhedral in form, and are molded strongly on plagioclase laths. They exhibit simple twinning (twin plane  $||(100)\rangle$ , and usually have extremely fine exsolution lamellae ||(001). When both twinning and the exsolution lamellae occur in the one crystal the well known herringbone structure results. Observations on the universal stage indicate that the pigeonite and augite are present in approximately equal proportions. The pigeonite is usually uniform in composition but the augite commonly has a core of variable size, which has a 2V averaging about 7° greater than the surrounding augite.

Pyroxenes (3) and (3A) represent the coexisting augite and pigeonite respectively from the normal, medium grained, quartz dolerite from the center of the Red Hill intrusion in Snug River (specimen M210). Except for an increase in grain size, and a decrease in proportion to approximately one fifth of the rock by volume, the pyroxenes are very similar in appearance and form to those in specimen (M212), just described. The pyroxenes have a distinct brown color and are not pleochroic. In some cases pigeonite and augite are intergrown with one another; where one pyroxene completely encloses the other, pigeonite is invariably in the core. Fine exsolution lamellae are usually present in both clinopyroxenes. The pigeonite from this rock is generally unzoned, except for the presence, in some cases, of a relatively thin outer rim. The optic angle shows considerable variation (Table 1) but the augite has a remarkably constant 2V, with zoning essentially absent.

Pyroxene (4) is the augite and (4A) the pigeonite from the dolerite immediately below the fayalite granophyre. This rock (M395) is about the most acid dolerite in which a member of both the augite and pigeonite series coexist. Because pigeonite is present in small amounts it was not possible to separate enough for analysis, so it was necessary to determine it optically (Table 3). Specimen (M395) is similar to the dolerite from the summit of Mt. Wellington (Edwards, 1942), and Muir (1955, p. 562) has plotted analyses of the coexisting augite and pigeonite phases from this rock; the compositions of which lie very close to those from specimen (M395) (see Fig. 8).

The pyroxenes from specimen (M395) closely resemble those of specimen (M210) but they are generally of slightly coarser grain size. They are a purplish brown color, but in some cases they have a thin mantle of pale green pyroxene. The augite is mostly unzoned, but may have a thin rim which has a 2V up to 10° greater than the core. The associated pigeonite is also fairly uniform, and has a 2V of about 12° in the plane ||(010). As in the previously described clinopyroxenes simple twinning on (100) and fine exsolution lamellae ||(001) are present.



FIG. 8. Comparison of the Red Hill pyroxene trend with the compositions of pyroxenes from other slowly cooled tholeiitic intrusions.

With further fractionation the magma passed from the two-pyroxene field into that in which only one pyroxene forms, by the pigeonite ceasing to crystallize. The pyroxene of the augite series continues to crystallize throughout the fayalite granophyre and granophyre, and becomes progressively enriched in Fe and slightly enriched in Ca with fractionation.

The ferroaugite (5) was separated from the fayalite granophyre (M12) from Red Hill, and is the only pyroxene phase present in the rock. The ferroaugite occurs as anhedral to prismatic crystals which are usually molded strongly on plagioclase laths. Although normally occurring as independent crystals, in some cases several grains have formed adjacent to one another to produce large glomeroporphyritic plates. The pyroxene is purplish brown in color, and is commonly partially rimmed by a pale green variety whose 2V is 5° to 8° higher than the fairly uniform cores. Twinning is not developed, but thin continuous exsolution lamellae  $\|(001)$  are usually present.

## PYROXENES IN A TASMANIAN DOLERITE

The change from the ferroaugite (5) of the fayalite granophyre to the ferrohedenbergite (6), which is typical of the granophyre, takes place over a vertical distance of some 200 feet in the Red Hill dike. The pyroxene in the granophyre, as noted above, assumes an elongate, feathery, appearance. Commonly the crystals consist of an irregular intergrowth of two distinct varieties of pyroxene; one is pale purple, the other pale green, and both are faintly pleochroic. When intergrown the two varieties have the same optical and crystallographic orientation. However the refractive indices of the green variety are about 0.001 lower than those of the purple. Minute iron ore inclusions occur in some crystals, particularly in the green variety. The fine exsolution lamellae ||(001), so common in the less Fe-rich pyroxenes of the intrusion, are rarely present in the ferrohedenbergite, and simple twinning is never developed. The ferrohedenbergites occurring in other granophyres are very similar to the analyzed pyroxene, but in some rocks the green variety tends to predominate.

Wager and Deer (1939) and Muir (1951) record the presence of two pyroxenes, one brown and the other green, in some of the latest differentiates of the Skaergaard intrusion. Muir shows that both pyroxenes are ferrohedenbergites containing very little Mg and that their compositions differ by only a few mol per cent. Wager and Deer suggested from the textural relations that the green variety has arisen by inversion of iron-wollastonite and Muir follows this interpretation. The brown pyroxene is considered to be a primary phase and, in some cases, crystallizes in optical continuity with the green variety. Poldervaart (1944) also observed two distinct varieties of pyroxene in granophyre from the New Amalfi Sheet.

In the Red Hill granophyres there is no reason to suggest that either the green or purple pyroxenes are other than primary phases; apart from the color and slight differences in optical properties the two pyroxenes are very similar. No obvious explanation is forthcoming to account for the occurrence of the two pyroxenes which have apparently crystallized in equilibrium with one another; conceivably the observed relations may be the result of a small immiscibility gap appearing in this part of the pyroxene system.

Thus during fractionation of the Red Hill magma both series of pyroxenes show a progressive change in composition towards more Ferich varieties. In the Ca-rich pyroxene series Fe<sup>2</sup> continually replaces Mg throughout the whole sequence, and during the early and middle stages of fractionation Fe<sup>2</sup> is also replacing Ca to some extent, since the Ca content of these pyroxenes decreases in amount from about 40% of the total Ca+Mg+Fe to about 31%, at the limit of the two-pyroxene field.

However in the late stages of fractionation the Ca content steadily increases in amount to over 41% in the ferrohedenbergite of the granophyre, so that in addition to replacement of Mg by Fe<sup>2</sup>, replacement of Mg by Ca also takes place.

The composition of the Ca-poor pyroxene during fractionation changes progressively by replacement of Mg by Fe<sup>2</sup>, until the cessation of crystallization of the pigeonite at the limit of the two-pyroxene field. There is apparently little variation in the Ca content of these pyroxenes except that the orthopyroxene probably contains about  $3\frac{1}{2}\%$  Ca of the total Ca+Mg+Fe (Poldervaart and Hess, 1951, p. 481), whereas the pigeonite contains about 10% Ca. Further analyses of pyroxenes of the Ca-poor series from the Red Hill intrusion would be extremely valuable in tracing in more detail, the variation in composition within this group during fractionation.

# Comparison of the Red Hill Trends with the Trends in other Intrusions

A considerable literature now exists on the pyroxenes from moderately slowly cooled saturated basic intrusions, but the Skaergaard body is the only one in which the variation in composition of the pyroxenes has been traced throughout the fractionation of the magma (Muir, 1951; Brown, 1957). The analyzed pyroxenes from several of these intrusions, including Skaergaard, are plotted in Fig. 8, together with the Red Hill pyroxenes; the similarity in trend is most striking, particularly between Skaergaard and Red Hill. The Red Hill pyroxenes of the augite series have a slightly lower Ca content than the Skaergaard pyroxenes, but, as in Skaergaard (Brown, 1957), there is a minimum in the Ca content at the limit of the two-pyroxene field. At this stage there is a change from a gradual decrease in Ca to one of gradual Ca enrichment. An important point, which holds for Skaergaard also, is that there is no evidence for any marked compositional break, in the augite series, at the limit of the two-pyroxene field.

The trend with fractionation in the Ca-poor pyroxene series is also very similar to that of Skaergaard. The crystallization begins with an Mg-rich orthopyroxene, which gradually becomes more Fe-rich, and then at an Mg:Fe ratio of approximately 70:30 gives way to pigeonite, which itself becomes progressively enriched in Fe during fractionation, until the limit of the two-pyroxene field is attained, when it ceases to crystallize.

The variation in composition of the Red Hill pyroxenes during fractionation also agrees in general with the trends proposed by Poldervaart and Hess (1951), who collected data from a number of different intru-

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sions, at several fractionation stages, to give the course of crystallization of pyroxenes within a single, strongly fractionated, basaltic body.

# THE LIMIT OF THE TWO-PYROXENE FIELD

It has been long established that a single pyroxene phase of the augite series crystallizes during the late stages of fractionation of tholeiitic basaltic magma, instead of both a Ca-rich and a Ca-poor phase, which crystallize together in cotectic equilibrium in the early and middle stages. In the Red Hill intrusion the limit of the two-pyroxene field occurs at an Mg: Fe ratio of about 40:60 in the pyroxenes; in Skaergaard the corresponding ratio is about 50:50, and Poldervaart and Hess (1951) give the value of 45:55 for tholeiites in general.

Several explanations have been advanced to account for the cessation of crystallization of the Ca-poor pyroxene phase. Poldervaart and Hess (1951, p. 479) suggested that there may be reaction of the pigeonite with the liquid to form a fayalitic olivine. At essentially the same stage as the pigeonite disappears in the Red Hill intrusion a favalitic olivine makes its appearance as a primary phase. There is no petrographic evidence of a reaction relation between the two minerals: the olivine has usually crystallized as discrete, large grains, not associated with pyroxene. It appears that the fayalite, rather than causing the cessation of crystallization of the pigeonite, has begun to form at this stage because of the disappearance of the pigeonite, owing to the marked absolute enrichment in Fe as well as the very strong enrichment in Fe relative to Mg in the liquid. Muir (1954, p. 384) concludes from his studies of Skaergaard, Beaver Bay and New Amalfi pyroxenes that the disappearance of Ca-poor pyroxene could not be due to a reaction relation with fayalitic olivine, and Brown (1957, p. 525) also arrives at the same conclusion as regards the Skaergaard intrusion.

The laboratory investigations of Bowen and Schairer (1935) show that hedenbergite and ferrosilite form a solid solution series with a mimimum. Hess (1941) developed the idea proposed by Tsuboi (1932) that at the limit of the two-pyroxene field a solid solution with a minimum forms, so that only a single pyroxene phase crystallizes with continued fractionation. If this were the correct explanation it would be expected that the compositions of the augite and pigeonite phases would converge as the limit of the two-pyroxene field was approached. However the data from Skaergaard (Muir, 1951; Brown, 1957), and now from the Red Hill intrusion, shows that no such convergence of the compositions takes place; in fact the trend in the augite series is away from the pigeonite at the limit of the two-pyroxene field. Therefore this explanation does not appear to satisfy the observed facts.

A third alternative was proposed by Muir (1954, p. 384), who suggested that, instead of the solidus surface dipping below the liquidus at the limit of the two-pyroxene field to produce a solid solution with a minimum, the liquidus minimum, which intersects the solvus, migrates toward the Ca-rich side of the solvus and passes beyond it, so that only a single Ca-rich pyroxene would then form. Such a mechanism can account for the disappearance of the pigeonite, and the continuity in the crystallization of the pyroxenes of the augite series, without any major change in trend, when the limit of the two-pyroxene field is reached.

# EXSOLUTION AND INVERSION PHENOMENA IN THE PYROXENES

When pyroxenes, which have crystallized from tholeiitic basaltic magma, are cooled moderately slowly, exsolution or unmixing of one pyroxene phase from another may take place, leading towards the attainment of a more ordered state, and is the result of the decrease in stability of one component in the other with decreasing temperature (Hess, 1941; Edwards, 1942; Poldervaart and Hess, 1951; Brown, 1957).

Edwards (1942, p. 584, p. 587) noted the presence of a pronounced parting || (001) in both the pigeonite and augite of the Tasmanian dolerites. Under high magnification it is found that this parting is produced by very fine exsolution lamellae; Muir (1955, p. 562) recognized such lamellae in the ferroaugite from the summit of Mt. Wellington. In both the augite and pigeonite these lamellae are very similar; they range in thickness from 0.0005 to 0.002 mm., with exceptional lamellae up to 0.003 mm.; they are spaced from 0.003 to 0.01 mm. apart, and constitute about 15 to 20% of each crystal. The lamellae have an orientation very similar to that of the host clinopyroxene, making them difficult to distinguish. They can be detected in practically all grains which are suitably oriented in the thin section, and usually occur throughout a crystal.

The work of Hess (1941) and of Poldervaart and Hess (1951) indicates that the lamellae in augite are pigeonitic in composition, whereas those occurring in pigeonite are composed of augite, and this has been confirmed by an x-ray study of an augite from Mt. Wellington by Bown and Gay (1959), who have shown that the lamellae are in fact composed of pigeonite. There is no evidence to suggest that the exsolved pigeonite in the augite crystals has inverted to orthopyroxene, so that the exsolution probably took place at a temperature above the pigeonite-orthopyroxene inversion curve (Fig. 7).

In the Red Hill intrusion exsolution lamellae occur in the pigeonite right up to the stage when it ceases to crystallize, at the limit of the twopyroxene field. In the augite series lamellae are present in all the pyroxenes up to and including the ferroaugite of the fayalite granophyre, but

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are generally absent from the ferrohedenbergite of the granophyre; the temperature at which these more Fe-rich pyroxenes crystallized must have been too low for any exsolution to take place, because of the relatively slow rate of diffusion at these temperatures. In addition it is probable that no pyroxene of the pigeonite series is stable in this composition field.

In the Red Hill intrusion the pigeonite contained in dolerites occurring in a zone up to 200 feet from the contacts, has, in some cases, partly or wholly inverted to orthopyroxene on cooling, because the temperature had fallen to below the pigeonite-orthopyroxene inversion curve (Fig. 7), into the stability field of orthopyroxene. Hess (1941) first recognized this phenomenon and independantly Edwards (1942) noted it in the lower parts of the Tasmanian dolerite sills.

In many cases the pigeonite has only partially inverted, so that commonly the parent pigeonite and the secondary orthopyroxene occur together in the one crystal. The boundary between the two phases is always sharp, if irregular, and in some cases the orthopyroxene ends abruptly along an augite exsolution lamellar in the pigeonite. The secondary orthopyroxene usually has uneven extinction, and contains the exsolved augite as fine lamellae, which are the continuation, and of the same thickness, as those occurring in the adjacent uninverted pigeonite (Figs. 9, 10). The lamellae in the orthopyroxene are much more obvious than those in the pigeonite, because in the former their orientation is quite different from the orthopyroxene, whereas in the pigeonite the lamellae of augite have a very similar orientation to that of the host.

According to Poldervaart and Hess (1951, p. 482) pigeonite crystallizes with some 9.5% Ca<sup>2</sup> ions of the total (Mg<sup>2</sup>+Fe<sup>2</sup>+Ca<sup>2</sup>), although the analyzed pigeonite (3A) from specimen (M210) appears to contain about 10.8% of the Ca<sup>2</sup> ion. Orthopyroxene, on the other hand, can accept only about  $3\frac{1}{2}\%$  Ca<sup>2</sup> ion into its structure, so that when pigeonite inverts to orthopyroxene the excess Ca<sup>2</sup> is exsolved in the form of augite lamellae or blebs. However the pigeonites in the Tasmanian dolerites have exsolved much of the Ca in the form of augite lamellae before the inversion to orthopyroxene, so that generally the exsolution lamellae in the secondary orthopyroxene are related to the parent pigeonite rather than to the orthopyroxene.

Further confirmation that orthopyroxene with well developed augite lamellae resulted from the inversion of pigeonite is provided by the preservation of the herringbone twin structure of the pigeonite (Figs. 9, 10).

Poldervaart and Hess (1951, p. 482) contend that "in the majority of cases of inversion of pigeonite to orthopyroxene, the orthopyroxene will



Fig. 9. Photomicrograph of pigeonite which has partially inverted to orthopyroxene. Some uninverted pigeonite showing a herringbone twin is present in the upper part of the field. The twin plane is (100) and the exsolution lamellae are parallel to (001), along which alteration has taken place. The remainder of the crystal is orthopyroxene. From quartz dolerite (specimen M212), about 40 feet from the western contact of the Red Hill Dike, Snug River, Plane light, scale mark is 1 mm. in length.

develop in such an orientation that it retains the b and c crystallographic axes of the parent pigeonite," but in the Red Hill intrusion this rarely occurs; an observation also made by Brown (1957) in his study of the Skaergaard pyroxenes. In the contact zones of the Red Hill dike, pigeonite commonly mantles primary orthopyroxene and assumes an orientation such that the b and c axes of the orthopyroxene are retained. If the pigeonite has subsequently inverted to orthopyroxene on cooling, the orientation of this secondary orthopyroxene, in some cases, is the same as the primary orthopyroxene, in agreement with Poldervaart and Hess' observations, but usually the orientation assumed is quite different. Also it is not uncommon to observe that a single pigeonite crystal, on inversion, has given rise to two or more areas of orthopyroxene which have different orientations; therefore even if one such area retained the b and c axes of the parent pigeonite the other(s) could not.

To further test the statement of Poldervaart and Hess a number of crystals of pigeonite, which had partially inverted to orthopyroxene, were plotted stereographically. In some cases the orientation of the orthopyroxene in relation to the parent pigeonite was quite random; in



FIG. 10. Same field as Fig. 9, but with crossed nicols. Note well developed exsolution lamellae in orthopyroxene, which are parallel to (001) of the original pigeonite. Relict twin plane of pigeonite preserved in secondary orthopyroxene. The orthopyroxene free of exsolution lamellae in the lower part of the field is probably primary.

other cases a relationship existed and the following orientations have been found:

c orthopyroxene = c pigeonite plane ab orthopyroxene contains b pigeonite

 $\begin{cases} b \text{ orthopyroxene lies in plane } ac \text{ pigeonite} \\ plane & ac \text{ orthopyroxene contains } b \text{ pigeonite} \end{cases}$ 

 $\begin{cases} a \text{ orthopyroxene lies in plane } ac \text{ pigeonite} \\ plane bc \text{ orthopyroxene contains } b \text{ pigeonite} \end{cases}$ 

Thus the Red Hill orthopyroxenes, which have resulted from the inversion of pigeonite, exhibit a variety of orientations relative to the parent pigeonite. In a few cases the orthopyroxene retains the b and c axes of the parent pigeonite; generally, however, the orientation is random, although it is not uncommon to find that one crystallographic axis of the secondary orthopyroxene lies in a plane defined by two of the crystallographic axes of the parent pigeonite, and a plane of the orthopyroxene contains a crystallographic axis of the pigeonite.

The pigeonite only inverts to orthopyroxene in the marginal zones of the intrusion. These pigeonites, which are Mg-rich, have crystallized at a temperature just above the pigeonite--orthopyroxene inversion curve (Fig. 7), and with cooling have been able to invert to orthopyroxene, because of the relatively fast rate of the inversion reaction at this temperature. Nevertheless, even in these rocks, less than half of the pigeonite has inverted, suggesting that the rate of cooling was such that the inversion could only be partially completed before the temperature decreased to a value at which it became too sluggish a reaction to take place. With increasing fractionation, away from the contacts of the intrusion, the pigeonite became progressively enriched in Fe and probably crystallized at an increasingly greater temperature above the inversion curve. By the time this pigeonite had cooled sufficiently to cross the inversion boundary, into the orthopyroxene stability field, the rate of the inversion reaction had become too slow, relative to the rate of cooling of the rock, because of the lower temperature of the phase boundary, for inversion to take place at all. Even in the central parts of the intrusion where the rate of cooling would have been the slowest, the inversion reaction has been too sluggish to occur.

Both the primary orthopyroxene and that which has resulted from the inversion of pigeonite, in some cases, contain exsolution lamellae of augite which are related to the orthopyroxene structure. These lamellae are very fine and of a similar thickness to those in the pigeonite, and are developed ||(100) of the host orthopyroxene. The lamellae are sporadically developed, even in the one crystal, and are not nearly as regular as those which occur in the clinopyroxenes. These augite lamellae have been exsolved from the primary or secondary orthopyroxenes as they cooled.

## SUMMARY AND CONCLUSIONS

At the time of emplacement of the dolerite magma in the Red Hill intrusion an Mg-rich orthopyroxene (Of<sub>15</sub>) was crystallizing, and after emplacement crystallization of this mineral continued for a short time until its composition reached Of<sub>30</sub>, when pigeonite with approximately the same Mg: Fe ratio began to separate instead of the orthopyroxene. The pigeonite continued to crystallize with fractionation, and became progressively enriched in Fe<sup>2</sup> relative to Mg, with the Ca content remaining essentially constant. At an Mg: Fe ratio of about 40:60 the pigeonite ceased to crystallize at the limit of the two-pyroxene field, perhaps as the result of the liquidus minimum of the pyroxene system migrating to the Ca-rich side of the solvus. More analyses of the Ca-poor pyroxenes are obviously desirable but it is believed that the main trend has been demonstrated.

A member of the Ca-rich pyroxene series crystallized during the whole

of the cooling history of the Red Hill magma, except for the very early stages, just prior to intrusion, when only orthopyroxene was separating. The Ca-rich pyroxene crystallized in cotectic equilibrium first with orthopyroxene, adjacent to the chilled contacts, and then with pigeonite, until the latter ceased to form, when the Ca-rich pyroxene continued to crystallize independently in the more acid rocks. During fractionation the composition of the Ca-rich pyroxene changed progressively by successive replacement of Mg by Fe<sup>2</sup> with some variation in the Ca content. In the early and middle stages of fractionation the Ca content decreased steadily from about 40 to 31% of the total Ca+Mg+Fe, followed by a steady increase in the amount of Ca in the late stages to over 41% in the ferrohedenbergite of the granophyre.

The trend of crystallization in both pyroxene series is strikingly similar to that of the Skaergaard intrusion, but the pyroxenes of the augite series of Red Hill are always slightly lower in Ca than the corresponding pyroxenes from Skaergaard.

In both the Ca-poor and Ca-rich clinopyroxenes very thin exsolution lamellae parallel to (001) occur, and are the result of unmixing of one pyroxene phase from another owing to the decrease in stability with lowering of temperature. The lamellae in pigeonite are believed to be augitic in composition and those in the augite of pigeonitic composition. Exsolution lamellae are present in the pigeonite series right up to the stage when it ceases to crystallize, and in the augite series lamellae occur in all the pyroxenes up to and including the ferroaugite of the fayalite granophyre, but are generally absent from the ferrohedenbergite of the granophyre. The lack of exsolution lamellae in this Fe-rich pyroxene is probably the result of the relatively low temperature of crystallization and also that possibly no pyroxene of the pigeonite series is stable in this composition field.

In a zone up to about 200 feet from the chilled contacts of the Red Hill intrusion some of the pyroxene has partially or completely inverted to orthopyroxene. Elsewhere in the intrusion inversion has not taken place. This is probably related to the fact that the pigeonite in the marginal zones has crystallized close to the inversion curve and that the inversion rate is quite rapid at this relatively high temperature. In the more strongly fractionated rocks the pigeonite is more Fe-rich and has probably crystallized at a temperature somewhat above the inversion curve and on cooling, when passing into the orthopyroxene stability field the inversion reaction has been too slow as compared with the rate of cooling for it to take place.

The orthopyroxene resulting from the inversion of pigeonite rarely retains the b and c axes of the clinopyroxene but generally the orientation

is random, or else one crystallographic axis of the secondary orthopyroxene lies in a plane defined by two of the crystallographic axes of the parent pigeonite and a plane of the orthopyroxene contains a crystallographic axis of the pigeonite.

The recalculation of the chemical analyses of the pyroxenes indicates that in four out of the five cases some  $Ti^4$  and/or  $Fe^3$ , in addition to  $Al^3$ , must replace Si in the tetrahedral position. With fractionation the minor constituents Ti, Mn and Fe<sup>3</sup> increase in amount whereas Al decreases, and in the analyzed coexisting augite and pigeonite Ti, Mn and Fe<sup>3</sup> are enriched in the pigeonite relative to the augite and Al is enriched in the augite.

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