CRYSTALLIZATION OF PYROXENES FROM BASALTS

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I. INTRODUCTION

Microscope studies of basalts from South Africa and the Pacific convince me that the pyroxenes of these rocks exhibit a gradual change in composition as crystallization proceeds.

The establishment of the course of crystallization of the natural pyroxenes is very important.

No one will deny the great significance of the reaction series of the plagioclases, and although the reaction series of the pyroxenes is fully as important, little more is known of it than the fact that a general enrichment in iron takes place as stated by Vogt, Fenner, and others.

The difficulty of establishing the course of these reaction series lies in the fact that very many mineral molecules enter into the natural pyroxenes. Many more data are required before it will be possible to determine the relations of different pyroxenes to different magmas;¹ but confining ourselves to basaltic magmas it is already possible to offer for consideration a general course of crystallization as far as the major constituents of the basaltic pyroxenes are concerned.

We know that the common pyroxenes of basalts are composed largely of metasilicates of magnesium, calcium, and iron. Neglecting for the present the minor constituents (the most important of which are sesquioxides and alkalies), the purpose of this paper will be to indicate the variations that take place between the three major silicates as pyroxenes crystallize from a basaltic magma.

To this end the minor oxides² in the pyroxene analyses have been neglected, the sum recalculated to 100 per cent and presented in

¹ Valuable data bearing on the formation of ferriferous pyroxenes are given in a recent synthetic study by Bowen, Schairer, and Willems: Am. Jour. Sci., 20, 405, 1930.

² Titanium dioxide is, however, reckoned with silica.
II. ABUNDANCE OF PIGEONITE

The first conclusion reached from the following brief survey of basaltic pyroxenes will be surprising to some petrographers. It will be shown that the pigeonite (i.e. pyroxene rich in clinoenstatite and/or clinohypersthene) is a very common mineral; indeed, after certain varieties of feldspar it seems to be the most abundant mineral of eruptive rocks.

Wahl4 pointed out the general occurrence of pigeonite in basaltic rocks twenty-five years ago, and Fermor5 concluded six years ago that pigeonite was the most abundant pyroxene in nature. But this fact has not yet received proper attention, especially in the English literature. This mineral affords a striking illustration of our lack of knowledge regarding the actual nature of the mineral phases in rocks.

When Winchell6 in 1900 examined pigeonite in the olivine diabase of Pigeon Point, Minnesota, he felt puzzled about the optical properties of this mineral, and concluded eventually that: "The abnormal optical properties... can scarcely be attributed to the chemical composition." That much was known then about the most abundant mafic mineral in nature. And even today very little attention is given to this mineral species. In standard textbooks on petrography and mineralogy little or nothing is said about it. Even the nomenclature is not established.

In 1900 Winchell6 called the mineral pigeonite.

In 1905 Rosenbusch proposed the name magnesiumdiopsid.7

In 1906 Wahl4, in his elaborate study, suggested the names: enstatitaugit, bronzitaugit, hypersthenaugit, enstatidiopsid, etc.

In 1906 Lacroix8 designated it clinoenstatite or clinohypersthene; but later9 he adopted Winchell's pigeonite.

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4 Also expressed as Hy, En, Wo, respectively.
6 A. N. Winchell, Am. Geol., 26, 1900, p. 203.
9 A. Lacroix, Minéral France, IV, 1910, p. 767.
It seems to me that a mineral, or rather a mineral series, of such eminent importance should have a short, concise name, and I am therefore in agreement with Winchell and Lacroix in selecting the name pigeonite for all pyroxenes of small axial angle.

III. PYROXENES OF THE PACIFIC

Within the vast Intra-Pacific petrographic province, basaltic rocks abound, and basaltic pyroxenes are encountered both as phenocrysts and as products of later crystallizations.

Chemical analyses of two Pacific pyroxenes are on record.

1. Early-formed crystals of an olivine basalt from Haleakala, Maui, have been studied by Washington and Merwin.11

2. Pyroxenes of later crystallizations from a basalt of Hiva Oa, Marquesas, have been analyzed by me.12

The results of the chemical analyses, recalculated in the manner described above, are:

<table>
<thead>
<tr>
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<th>1</th>
<th>2</th>
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<tbody>
<tr>
<td>Hy</td>
<td>8</td>
<td>21</td>
</tr>
<tr>
<td>En</td>
<td>42</td>
<td>50</td>
</tr>
<tr>
<td>Wo</td>
<td>49</td>
<td>29</td>
</tr>
</tbody>
</table>

Taking these two analyses as representative of the composition of early- and later-formed pyroxenes, respectively, the course of crystallization must proceed along the line 1–2 of Fig. 1.

Microscope studies of more than 100 thin sections of Pacific rocks show that the axial angles of the pyroxene phenocrysts are 50°–60°, whereas the pyroxenes of the groundmass exhibit smaller axial angles varying from 0° to 50°. It is thus obvious that the general trend of the crystallization within the whole eruptive province runs from early-formed diopsidic augites to pyroxenes rich in clinoenstatite and/or clinohypersthene of later crystallizations.13

In most Pacific rocks two or more generations of pyroxenes are encountered; in some of the rocks they form a continuous series of pyroxenes.

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10 References to my previous paper, "Mineralogical Petrography of Pacific Lavas," Am. Jour. Sci., 21, 377–405, 1931, etc. will be made as "Pacific Lavas" or only "P.L." Washington's papers, "Petrology of the Hawaiian Islands" I to VI, Am. Jour. Sci., 5, 465; 6, 100, 338, 409, 1923; 12, 336, 1926; 15, 199, 1928, will be referred to as (I), (II), (III), (IV), (V), (VI).


13 Such pyroxenes will be called pigeonites.
mix-crystals, but in others there is no such transition, the phenocrysts being distinctly different from the pyroxenes in the groundmass. A few examples follow.

(3) *Olivine basalt*, south of Kaala, Kohala, Hawaii. Pyroxene phenocrysts (4.7 per cent of the rock) are commonly zoned, \((+)^{2}V \approx 58^\circ\); the refractive index \(\beta\) is about 1.69. The groundmass pyroxene makes up 40 per cent of the rock; the axial angle varies from 40° to 50°.

(4) *Olivine basalt*, Nihoa, Leeward Islands. Pyroxene phenocrysts (4.5 per cent of the rock) show the following properties: \((+)^{2}V = 58^\circ \pm 2^\circ\). \(\alpha = 1.680, \beta = 1.687, \gamma = 1.712; \pm 0.003\). Z: \(44^\circ\). The axial angle of the groundmass pyroxene is small, 20°–40°, but the indices of refraction are essentially the same as for the phenocrysts.

(5) *Basalt*, Kawaihae Gulch, Kohala, Hawaii. Pyroxene microphenocrysts, constitute 3 per cent of the rock and show the following properties: \((+)^{2}V = 58^\circ\), \(\alpha\) varies from 1.685 to 1.695, \(\beta = 1.690 - 1.700, \gamma = 1.720 - 1.730\). The groundmass pyroxenes make up 39 per cent of the rock; axial angle = 30°–40°; \(\beta = 1.69 - 1.70\).

These three rocks have been analyzed by Washington, and the mode or actual mineral composition has been determined by me. In this way it is possible to calculate with a fair degree of accuracy the average composition of the pyroxenes present, and knowing also the proportion of phenocrysts to groundmass, and also the optical properties of the pyroxenes of both generations, one can offer a good estimate of the composition of each of them, thus:

<table>
<thead>
<tr>
<th></th>
<th>3</th>
<th>4</th>
<th>5</th>
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<tbody>
<tr>
<td></td>
<td>Phenocr.</td>
<td>Gr. mass</td>
<td>Phenocr.</td>
</tr>
<tr>
<td>Hy</td>
<td>8</td>
<td>27</td>
<td>6</td>
</tr>
<tr>
<td>En</td>
<td>45</td>
<td>52</td>
<td>44</td>
</tr>
<tr>
<td>Wo</td>
<td>47</td>
<td>21</td>
<td>50</td>
</tr>
</tbody>
</table>

\(^{14}\) Nos. 3 and 5 in (I), p. 487, columns 2 and 1, respectively. No. 2 in (V), p. 344, column 3.

\(^{15}\) Nos. 3, 4, and 5 are Nos. 14, 13 and 44, respectively, of my paper, "Pacific Lavas." The underlying data for the calculation of the composition of these three and the following pyroxenes are also to be found in that paper.

\(^{16}\) Pyroxene constitutes between 40 and 50 per cent of these rocks, it is the only essential ferromagnesian mineral, consequently the inferred composition may be taken as essentially correct.
In the Pacific one also finds rocks carrying only one generation of pyroxenes. Some of these rocks have been analyzed and the modes have been established, and finally, the composition of the pyroxenes has been calculated.

The following rocks carry pyroxene mostly as phenocrysts:

(6) and (7). Basanite, Haleakala, Maui, Nos. 37 and 31 in "P.L." Analyses in (VI), p. 211, Cols. 5 and 7.

(8) Picrite basalt, Kaula Gulch, above Ookala, Mauna Kea, No. 28 of "P.L." Anal. in (I), p. 500, Col. 3.

(9) Limburgite basalt, Pimoa Cone, Maui, No. 28 of "P.L." Anal. in (VI), p. 214, Col. 2.

(10) Olivine basalt, Nonopapa, Niihau, No. 12 of "P.L." Anal. in (V), p. 332, Col. 4.

The compositions of the pyroxenes of these rocks are:

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<tr>
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<th>6</th>
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<th>9</th>
<th>10</th>
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<tbody>
<tr>
<td>Hy</td>
<td>13</td>
<td>15</td>
<td>17</td>
<td>22</td>
<td>25</td>
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<tr>
<td>En</td>
<td>38</td>
<td>35</td>
<td>36</td>
<td>28</td>
<td>22</td>
</tr>
<tr>
<td>Wo</td>
<td>49</td>
<td>50</td>
<td>46</td>
<td>50</td>
<td>53</td>
</tr>
</tbody>
</table>

Fig. 1. Pyroxenes from the Pacific.

- Phenocrysts
- Groundmass pyroxene

For explanation see text.
In the following rocks the pyroxene occurs in the groundmass.

(11) Olivine basalt, W. end of Taiohae, Nukuhiva, Marquesas, No. 3 in “P.L.” Analyses in Washington, Barth, and Keyes, Petrology of the Marquesas Islands. (To be published).


(13) Picrite basalt, Nihoa, No. 27 of “P.L.” Anal. in (V), p. 344, Col. 4.

(14) Basalt from crater wall, Kilauea, No. 45 in “P.L.” Anal. in (III), p. 342, Col. 2.


(17) Gabbro included in basalt, summit of Hualalai. Anal. in (II), p. 104, Col. 3.

(18) Labradorite basalt, Nihoa, No. 53 of “P.L.” Anal. in (V), p. 344, Col. 2.

The compositions of the pyroxenes in these rocks are:

<table>
<thead>
<tr>
<th></th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hy</td>
<td>19</td>
<td>15</td>
<td>17</td>
<td>24</td>
<td>27</td>
<td>16</td>
<td>27</td>
<td>.39</td>
</tr>
<tr>
<td>En</td>
<td>40</td>
<td>50</td>
<td>58</td>
<td>50</td>
<td>54</td>
<td>33</td>
<td>36</td>
<td>.32</td>
</tr>
<tr>
<td>Wo</td>
<td>41</td>
<td>35</td>
<td>25</td>
<td>26</td>
<td>19</td>
<td>50</td>
<td>37</td>
<td>29</td>
</tr>
</tbody>
</table>

A review of the data so far obtained has been plotted in the composition diagram (Fig. 1). The numbers used in the diagram are those in the Tables I to IV.

IV. PYROXENES OF THE KARROO DOLERITES

In the Karroo dolerites of South Africa the pyroxenes form a continuous series of mix-crystals which has been precipitated simultaneously with the plagioclase series of the feldspars. One can not discriminate, therefore, between phenocrysts and groundmass, and the only way to determine the course of crystallization is by studying the zoning. The rocks examined by me have been chemically analyzed by Radley, and thus the average composition of the pyroxenes can be calculated.\(^{17}\)

\(^{17}\) The underlying data for these calculations are given in a joint paper by Daly and the author. Dolerites associated with the Karroo System, etc. Geol. Mag., 67, 1930, p. 97.
In these rocks the pyroxenes are conspicuously zoned, so it is difficult to obtain exact optical data. The mean index of refraction is always around 1.68, but a definite relationship to the size of the optic angle could not be established. Invariably the core has a larger axial angle than the surrounding shell, for example:

<table>
<thead>
<tr>
<th>Crystal from rock No. 2</th>
<th>Core</th>
<th>2V*</th>
<th>Z:c</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40°</td>
<td>23°</td>
<td>29°</td>
</tr>
<tr>
<td>Crystal from rock No. 1</td>
<td>Core</td>
<td>49°</td>
<td>35°</td>
</tr>
<tr>
<td></td>
<td>Medium layer</td>
<td>45°</td>
<td>35°</td>
</tr>
<tr>
<td></td>
<td>Border</td>
<td>0°</td>
<td>31°</td>
</tr>
</tbody>
</table>

* Extreme values are given.

It is thus obvious that the pyroxenes of these rocks are not homogeneous, but form a continuous series of mix-crystals, from diopside-rich to hypersthene-rich members. Fig. 2 presents graphically the course of crystallization of these pyroxenes.

V. DECCAN TRAPS

Another large petrographic unit of basaltic rocks is found in Deccan, India. As pointed out by Merwin, Washington, and Fermor, the pyroxene representing the main crystallization (groundmass) of these basalts is pigeonite.

My studies confirm this completely. All pyroxene in the groundmass exhibits a small to very small axial angle: frequently uniaxial crystals are met with, and in some cases the axial angle opens up again in a plane normal to the plane of symmetry. For example: Pyroxene from basalt of Katem quarries, Rajamundri, Madras.
This indicates a pigeonite very low in lime; indeed, only three other occurrences of a monoclinic pyroxene of such an extreme composition are on record.\(^\text{18}\)

The pyroxenes of these traps are very heterogeneous, values of the optic angle ranging from 0° to 40° are frequently found in the same thin section, even within the same mineral grain; but no regular zoning was observed. Several measurements indicate that the core is generally more calcic than the border, but no definite data can be given.

A study of the phenocrysts, however, is very instructive. Phenocrysts, or rather microphenocrysts, are very rare; indeed, in the strict sense of the word no phenocrysts at all occur; but here and there one can see relatively large crystals of pyroxene, often associated with feldspar laths, attaining a length of about one millimeter, as obvious products of an earlier crystallization of the basaltic magma.

In such crystals the axial angle is always around 60°. For example, the rock from the Katem quarries carries a few larger pyroxene grains showing (+) 2V = 57° ± 2°. Phenocrysts in a trap from Hingancy, Hyderabad, exhibit axial angles of from 50° to 60°, the mean index of refraction being around 1.70, (lowest observed index = 1.69, highest 1.73). The axial angle of the groundmass pyroxene of the same rock averages about 20°. Similar values are given by Fermor\(^4\) for pyroxene from the Bhusawal lavas (2V = 20°), and by Merwin\(^9\) on (groundmass) pyroxenes from traps of Chhindwara, Seoni, and Neemuch: axial angles range from very small up to 30° in the plane of symmetry, \(\alpha = 1.700–1.710\), \(\gamma = 1.725–1.735\).

From these data it becomes apparent that the earlier formed crystals are diopsidic, whereas those formed later are hypersthenic in composition.

More accurate data can be obtained from a chemical analysis


\(^{19}\) *Bull. Geol. Soc. Am.*, 33, 1922, p. 769.
made on a pyroxene from the groundmass taken from a trap at Kolhapur.\(^{20}\)

The analysis presented in terms of the usual silicate molecules may be compared with the phenocrysts of the aforementioned trap of Hingancy. The compositions are as follows:

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<tr>
<th></th>
<th>5</th>
<th>6</th>
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<tbody>
<tr>
<td></td>
<td>Phenocryst,(^*) Hingancy</td>
<td>Groundmass Pyroxene, Kolhapur</td>
</tr>
<tr>
<td>Hy</td>
<td>18</td>
<td>38</td>
</tr>
<tr>
<td>En</td>
<td>32</td>
<td>37</td>
</tr>
<tr>
<td>Wo</td>
<td>50</td>
<td>25</td>
</tr>
</tbody>
</table>

\(^*\) Approximate composition as estimated from the optical properties.

Fig. 2. 1, 2, 3, 4. Pyroxenes from Karroo the dolerites. 5, 6, 11. Pyroxenes from the Deccan traps. 7, 8, 9, 10. Pyroxenes from the Cape Verde Islands.  • Phenocrysts  • Groundmass pyroxene

For explanation see text.

As all the phenocrysts in the Deccan traps are very similar to this one (No. 5), while the groundmass pyroxenes generally approximate the above-stated composition (No. 6),\(^{21}\) these two types of pyroxenes may be taken as representing early-formed pyroxene and pyroxene of the groundmass of the basaltic magma. The course of crystallization of the pyroxenes is thus indicated by the line 5–6 in Fig. 2.

VI. CAPE VERDE ISLANDS

C. Doelter\(^{22}\) some fifty years ago made a comprehensive study of the pyroxenes of the rocks of the Cape Verde Islands. His method of investigation is more adequate than that of most petrologists, who usually confine themselves to the study of the phenocrysts, not taking the trouble to attack the more difficult task of examining the groundmass.

The following series of analyses (recalculated) indicates the course of crystallization of the pyroxenes in the basalts of these islands.

### Table VII

<table>
<thead>
<tr>
<th></th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
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</thead>
<tbody>
<tr>
<td>Hy</td>
<td>9</td>
<td>8</td>
<td>9</td>
<td>24</td>
</tr>
<tr>
<td>En</td>
<td>44</td>
<td>46</td>
<td>48</td>
<td>41</td>
</tr>
<tr>
<td>Wo</td>
<td>47</td>
<td>45</td>
<td>43</td>
<td>34</td>
</tr>
</tbody>
</table>

7. Very large augite crystals from dolerite.
8 and 9. Loose crystals.
10. Augite of the main crystallization (groundmass) of the olivine basalt.
(See Fig. 2 for a graphical representation.)

VII. OTHER ANALYTICAL DATA

As a further attempt toward establishing the general course of crystallization, chemical analyses of pyroxenes from different parts

\(^{21}\) It is worth noting that the analysis of the groundmass pyroxene from Kolhapur corresponds very closely to the normative composition of the pyroxene as calculated from the rock analysis. The normative compositions of other trap pyroxenes as well as of pyroxenes from the Oregon plateau basalts, have also been calculated, using Washington's analyses (Bull. Geol. Soc. Am., 33, 1922, p. 765), and they all are similar in composition to this one. The average normative composition of the Deccan pyroxenes as calculated from 11 analyses is: Hy = 31, En = 44, Wo = 25, and is presented by point 11 of Fig. 2.

\(^{22}\) C. Doelter, *Vulkane der Capeverden und ihre Produkte*, Graz, 1882.
of the world have been collected and recalculated in the way described.

Loose crystals and also large phenocrysts in basalts have been repeatedly analyzed, but only a few chosen at random among the more recent analyses have been recalculated and plotted in the diagram (Fig. 3). From these observations it is clearly shown that the phenocrysts generally are diopsidic augites.

Reliable analyses of groundmass pyroxenes are rare, but all of them, so far as known, indicate pyroxenes low in lime (pigeonites).

These features are clearly brought out by the graphic representation of Fig. 3, which shows that, throughout the world, the general course of the crystallization of basaltic pyroxenes is similar to that which was found to exist in the Pacific, South Africa, India and the Cape Verde Islands. Regarding the noteworthy occurrence of a lime-poor pigeonite as phenocrysts in a lava of Mull (circle 16), see discussion under topic VIII.

It may be added that on a pyroxene in a basalt from St. Paul, Pribilof Islands, Bering Sea, the following measurements were made:

<table>
<thead>
<tr>
<th>Phenocrysts</th>
<th>Groundmass pyroxene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core</td>
<td>border</td>
</tr>
<tr>
<td>$2V_\gamma$</td>
<td>$32^\circ$</td>
</tr>
<tr>
<td>$Z:c$</td>
<td>$44^\circ$</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Ca. 1.69</td>
</tr>
</tbody>
</table>

(Lowest observed index: 1.685, highest: 1.715.)

(VIII. BRITO-ARCTIC BASALTS)

In the widespread basaltic rocks of the Brito-Arctic province pigeonites have long been known. In an andesite from Mull even phenocrysts of pigeonite are encountered (plotted as No. 16, Fig. 3).

In Icelandic basalts Hawkes\(^{24}\) was the first to notice the presence of pigeonite, and later Holmes\(^{25}\) described this mineral from different basalts of the Arctic region.

From the basalts of Uifak (Greenland) Nicolau\(^{26}\) has described a lime-poor pyroxene which afterwards was re-examined by Wahl and identified as pigeonite (entered in Fig. 3 as No. 8).

From these descriptions it is difficult, however, to get an idea of the sequence of crystallization.


The following statements of Holmes seem to indicate a sequence opposite to that which has been found in other basaltic areas.

In Iceland olivine basalts from Onundafjord and Isafjord carry phenocrysts of pigeonite and in a basalt at Grundafjord a pigeonite "shades off on the borders and along terminations into augite. . . ."

But also the groundmass pyroxene is often said to be of the pigeonitic variety (Holmatindur, Eskifjord; Vágsfjord, Faeroes; etc.).

Also certain basalts from Spitzbergen, Franz Joseph Land, and Hooker Island carry, according to Holmes, pigeonite in the groundmass.

In the memoir of the rocks from the Mull district it is stated that "in some non-porphyritic olivine dolerites columnar augites have a core, now preferentially replaced by hornblende, which, no doubt, originally consisted of either enstatite augite, or rhombic pyroxene." But it seems to me that there is little reason for this conclusion; the original core could have been made up of olivine as well.

In a recent paper dealing with rocks of the same region Walker\(^27\) writes that the pyroxene is a monoclinic enstatite augite with 2V around 60°! Thus there seems to be some confusion in the nomenclature used by some British authors.

Be that as it may, phenocrysts of pigeonite seem to occur in different basalts of the Brito-Arctic province. Thin sections of these rocks unfortunately have not been available to me; I can only state that I have never seen true phenocrysts of pigeonite in any basalt from other parts of the world. One can sometimes observe larger crystals of pigeonite in basalts, but in such cases a closer examination always has shown that these crystals were originally olivine that has been changed over to a pyroxene in accordance with the well-known reaction principle of Bowen.\(^28\) Actually such basalts contain considerable amounts of both olivine and quartz, and the pyroxene is consequently, so to speak, still *in statu nascendi*, the reaction between magma and olivine being arrested before it was completed. Such lavas have been described by me from the Pacific.

The actual occurrence of pigeonitic phenocrysts in Brito-Arctic lavas might likewise be accounted for in the same way.

In agreement with the experimental studies of Bowen\(^29\) the pres-


ent survey indicates a complete series of solid solutions in the natural basaltic pyroxenes and consequently fails to demonstrate the discontinuity area proposed by Asklund. As shown by him, calculations of the normative composition of a great many pyroxenes indicate that iron-poor members of the diopside-clinoenstatite series should break down and form two different natural pyroxenes. According to his calculations the natural pyroxenes would have a rather complicated crystallization history. Under certain conditions enrichment even in lime might take place. These calculations suggest therefore an alternative explanation of the aforementioned occurrence of pigeonitic phenocrysts in Brito-Arctic basalts. More definite data of the mode of occurrence of the phenocrysts are, however, needed to settle this question.

Thanks are due to Dr. H. S. Washington for free use of his collections of rocks and thin sections, and to Dr. N. L. Bowen for criticism of the paper.

SUMMARY

Pigeonite is the most abundant pyroxene in volcanic rocks. Pyroxenes crystallizing from a basaltic magma exhibit a regular sequence of crystallization from diopsidic to hypersthenic, during which the content of MgSiO$_3$ may remain constant or increase slightly.

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30 B. Asklund, Petrology of the Stavsjö Area etc., *Sveriges Geol. Undersökning*, Ser. C, Årsbok 17, No. 6, Stockholm, 1925.