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PYROXENES OF COMMON MAFIC MAGMAS^{1,2}. PART 1

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Abstract

The pyroxenes of fine grained and coarse grained mafic intrusives and those of mafic extrusives are described. Hypotheses on the trend of crystallization of pyroxenes from basalts are reviewed. The investigation indicates that augite does not grade into pigeonite, but that pigeonite is a definite and distinct mineral variety. Augite and pigeonite may and do crystallize together in equilibrium with each other. Limited, rather than complete, solid solution exists in a portion of the clinopyroxene field. Pigeonite inverts on slow cooling to hypersthene and this inversion may be used as a point on a geological thermometer. Hypersthene inverted from pigeonite can be distinguished from hypersthene of primary crystallization. The temperature of basaltic intrusions does not exceed 1140° C. and normally is close to 1120° C.

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During a period of several years data have been collected on the chemical composition of pyroxenes, their optical properties, and the relations of pyroxenes to each other in a given specimen and in suites of specimens from the same occurrence. Though the primary purpose of this study

¹ Princeton investigations of rock forming minerals, No. 3.

² Presented before the Section of Volcanology, Am. Geophys. Union, April 1940.

was to correlate optical properties and chemical composition, certain interesting by-products resulted which are set forth in this paper.³

So far as the pyroxenes themselves are concerned only the common varieties have been investigated, those essentially composed of the Wo-En-Fs molecules with small to moderate amounts of trivalent oxides and titanium. Alkali pyroxenes, such as those with a considerable content of the acmite or jadeite molecule, have not been studied. The pyroxenes investigated all come from common igneous rocks—gabbros, norites, pyroxenites, diabases, basalts, andesites, etc.,—but not from such rocks as the lamprophyre dikes or markedly alkalic rock types. Broadly it might be said that this is a study of pyroxenes from normal basaltic magmas and their immediate products of differentiation, though it is quite possible that a few of the rocks considered are not differentiates of basalt.

NOMENCLATURE FOR COMMON CLINOPYROXENES

Before the clinopyroxenes can be discussed some agreement is desirable concerning a nomenclature for them. At present there is much confusion as to the meaning of such frequently used terms as augite, pigeonite, diopside, etc., and the literature is replete with obsolete and illdefined varietal names, the majority of which might with advantage be discarded and forgotten because they introduce wholly unnecessary complications. Aside from inadequate chemical and optical data on common clinopyroxenes, the confusion in nomenclature has been the greatest obstacle in the way of an understanding of the petrological relations of igneous pyroxenes to the rocks in which they occur and the magmas from which they were derived.

An attempt will be made here to define the common clinopyroxenes (exclusive of acmite and jadeite bearing varieties) in terms of chemical composition, following the general pattern laid down by Winchell for various mineral groups. Within this chemical classification present usage will be observed so far as is feasible, and the subdivisions between varieties will be made where possible on the basis of genetic significance.

The chemical classification for this group will be based primarily on the relative molecular percentages of Wo⁴ (CaSiO₃), En (MgSiO₃), and Fs (FeSiO₃) contained in the pyroxene and secondarily on other constituents. Present classifications as a rule make one large subdivision of the clinopyroxenes on the basis of Al₂O₃ content, or Al₂O₃+Fe₂O₃ content. To use the trivalent oxide content as a primary basis for classification of clinopyroxenes is objectionable on two grounds: first because

³ Chemical and optical data to be published separately.

⁴ It is not meant to infer that Wo as a wollastonite molecule exists in pyroxenes, but rather Wo, En and Fs are used in the chemical sense as in norms of rocks.

alumina is a comparatively minor constituent of the clinopyroxenes, and second because it has small effect on optical properties so that its presence or absence cannot now be determined without a chemical analysis. The latter objection is of much importance when it is considered that clinopyroxene is one of the commonest minerals of the earth's crust, and petrologists are constantly faced with the necessity of naming clinopyroxenes on the basis of optical investigations alone. From the practical point of view, disregarding the alumina content, in classifying clinopyroxenes, affects but slightly the common usage of augite now defined as an aluminous clinopyroxene since practically all natural clinopyroxenes falling within the Wo: En: Fs field suggested for augite in this paper are also aluminous. It does, however, restrict the use of augite to a slightly smaller field than its previous rather loose definition permitted. Pigeonites also contain trivalent oxides in about the same proportions as augites, but it is obviously advantageous to restrict the use of augite so that it will not include pigeonite. Diopside-hedenbergite clinopyroxenes, redefined here as those with Wo: En+Fs ratio near 1:1, rarely contain sufficient amounts of trivalent oxides to warrant classifying them as augite under the existing definition, so that except in rare instances there will be no conflict between the existing definition and the new one suggested here. In such rare cases where aluminian diopside-hedenbergite clinopyroxenes are encountered the writer would prefer to designate them by the above name rather than consider them augites since they depart considerably in composition from normal augites of gabbros, diabases, etc., and this departure is significant from the petrologic point of view.

The classification of common clinopyroxenes to be used in this paper is given in the figure below. The classification is based on the proportions of Wo, En and Fs, but it is specifically understood that augites and pigeonites contain moderate amounts of trivalent oxides as well.

Augites are the common pyroxenes of diabases, gabbros, norites, etc. They normally range near Wo_{40} , but the Wo content decreases somewhat with increase in Fs so that ferroaugites lie near Wo_{30} . According to the chemical classification adopted by Wager and Deer (1939), or the optical classification now used by many petrographers, the bulk of augite and ferroaugite would be considered as pigeonite. True pigeonites, however, represent a distinct mineral species which so far as is now known in all cases lies close to Wo_9 . The fact that pigeonite and augite or ferroaugite may crystallize together⁵ and in equilibrium in an igneous rock necessitates the limiting of pigeonite to the variety with a calcium silicate content of Wo_9 (2V=0 to a maximum of $<32^\circ$, augite and ferroaugite $2V>32^\circ$) rather than some arbitrary limit which would include part of

⁵ Discussed in a later part of this paper.

augite and ferroaugite. The actual limits in Wo for pigeonite here suggested are Wo_5 to Wo_{15} , to allow for possible variations not at present known.

The diopside-hedenbergite series is split into four parts based on Mg:Fe ratio. Salite and ferrosalite are inserted between the two end members. Salite is used in this sense by Winchell. The original salite from Sala, Sweden, however, would be classed as a diopside in this report be-



cause of its relatively high $CaMgSi_2O_6$ content. Salite has also been used to refer to clinopyroxenes with a basal parting ("salite parting"). The majority of natural occurrences of the diopside-hedenbergite pyroxenes are from contact metamorphic rocks and from veins. These crystallize at a considerable lower temperature than most igneous clinopyroxenes. In general (but with certain exceptions noted in the text) the Wo content decreases with increase in temperature of crystallization. The boundary, therefore, between salite and augite is placed at Wo₄₅ because most augites in igneous rocks contain less calcium silicate than Wo₄₅, and most contact metamorphic and vein salites more calcium silicate than Wo₄₅.

The remaining clinopyroxenes lie on either side of the diopside field.

For those below diopside, towards enstatite the name endiopside is given, a contraction of Wahl's little used enstatite-diopside. Pyroxenes in this field are rare but of sufficient genetic significance to warrant a distinctive name. All examples thus far examined by the writer contain substantial amounts of Cr_2O_3 (about 1 per cent). No name is given to those clinopyroxenes above the diopside field (containing excess $CaSiO_3$). As a rule these clinopyroxenes are also rich in TiO_2 and Al_2O_3 so it is questionable whether they can be dealt with in a classification based primarily on Wo:En:Fs ratios. Winchell⁶ suggests the presence of a $CaTiAl_2O_6$ molecule to account for these pyroxenes. It may be noted also that Barth (1931A) suggested the presence of this molecule and synthesized clinopyroxenes with up to ten per cent of the $CaMgTi_2O_6$ molecule in combination with diopside. In this latter case the Ti was considered to have replaced Si in the lattice rather than Mg as in the molecule given above.

To take care of certain varieties containing more than ordinary amounts of one of the nonessential elements, such terms as titanaugite, chrome-diopside, manganhedenbergite might be adopted from present common usage, or, if preferable, the adjectival forms suggested by the committee on nomenclature such as *manganoan* hedenbergite might be used.

As shown in Fig. 1 by dashed rather than solid lines, some of the composition limits of the various clinopyroxenes are left indefinite. No doubt as additional chemical data becomes available, modifications in the present classification will be necessary. A considerable portion of the entire field has been left blank. It is probable that further investigations will bring to light pyroxenes in some of these areas, but others are probably fields in which no natural clinopyroxenes will be found.

PIGEONITE-AUGITE RELATIONS

Pigeonite was defined by Winchell (1900) as a clinopyroxene with a small optic angle. It is redefined in this paper in terms of composition, but clinopyroxenes within the composition field of the definition have small optic angles, and all common clinopyroxenes of igneous rocks which lie outside of this field have larger optic angles so that the essential feature of Winchell's definition has been retained.

It is generally considered that a complete gradation from clinopyroxenes of pigeonitic composition to augites exists;⁷ assuming for the mo-

⁶ Personal communication.

⁷ Laboratory investigation of pyroxenes shows a solid solution series with a minimum for the system clinoenstatite-diopside (Bowen) and also a similar series for hedenbergite with clinoferrosilite (Bowen, Schairer and Posnjak), but pyroxenes intermediate between ment that such a gradation does occur, it would be convenient to place some upper limit on the optic angle of pigeonite above which value the pyroxenes would be considered to be augites. The writer suggests that a convenient limit would be $2V = 32^{\circ}$ in the plane parallel to (010). Those clinopyroxenes with the optic plane perpendicular to (010) are definitely pigeonites and the optic angles of these probably do not exceed 32° . The great majority of pigeonites in igneous rocks seem to have their optic plane perpendicular to (010). The orientation of the optic plane is often not given in the more recent literature.

In actual observations of optic angles on augites and pigeonites (excluding phenocrysts)⁸ from the same rock, a well defined gap appears to exist. The writer has examined a large number of such slides of rocks from various parts of the world. In practically all of them there is a gap in optic angle values between approximately $2V=30^{\circ}$ and $2V=40^{\circ}$. In a few cases augites with optic angles slightly below 40° , or pigeonites with optic angles slightly above 30° , were found. The normal optic angle range for augites is from 40° to 52° and the average about 46° .⁹ In the case of pigeonite the optic angle varies much more rapidly with change of composition (Wo content). The optic angles commonly range from $2V=30^{\circ}$? parallel to (010) through $2V=0^{\circ}$ to $2V=30^{\circ}$ perpendicular to (010). The average values would lie between $2V=0^{\circ}$ and $2V=25^{\circ} \perp$ to (010).

It is quite likely that the gap mentioned above might be shifted a few degrees one way or the other, or narrowed by the effects of non-essential minor constituents present in highly variable amounts in clinopyroxenes. Titanium is perhaps the most important of these.¹⁰

these two systems have not been investigated. Because of the laboratory data it has generally been assumed that a complete series of solid solutions existed between augite and pigeonite.

⁸ In this entire discussion phenocrysts are excluded from consideration since they are commonly of abnormal composition. This will be considered separately when the pyroxenes of effusives are taken up. The clinopyroxenes here under consideration are those of even grained rocks such as diabases or dolerites and the groundmass pyroxenes of such porphyritic rocks as basalts and andesites. The optic angles of the so called "augite" phenocrysts commonly lie between 55° and 60°.

⁹ Optic angles of augites which have cooled slowly and thus exsolved hypersthene as fine lamellae will be higher than those in the more rapidly cooled rocks—45° to 60°. Essentially the clinopyroxene host is changed in composition from augite towards a diopsidehedenbergite pyroxene and will have comparable optical properties. The bulk composition of this clinopyroxene plus its lamellæ will, of course, be the same as that of the original augite.

¹⁰ Most optic angle measurements are subject to an error of $\pm 1^{\circ}$. In some of the older references errors as high as 5° might be expected. Determinative errors will, therefore, tend to make the optic angle gap less well defined.

Examples of the occurrence of two clinopyroxenes in a single rock and of specific observations on optic angles of the two clinopyroxenes as made by various investigators, are given below. It is very common in the literature to find statements that the groundmass pyroxene of a basalt, or an andesite, has a highly variable optic angle, ranging continuously from $2V = \pm 50^{\circ}$ to $2V = 0^{\circ}$. Kuno (1936A) makes the following comment on the groundmass pyroxenes from andesites of the Hakone volcano, Japan: "... it is noted that the optical data of the groundmass *pigeonites* show that they tend to group in two types, viz., *pigeonite* with 2Vnearly 0° and that with 2V nearly 40°.¹¹ But since intermediate types are occasionally found, the above fact does not mean existence of miscibility limits in the composition range of pigeonite." As can be noted below *some* intermediate values are found but the actual observations themselves suggest that *all* intermediate values are not found.

Actual observations made by Kuno on andesites from Hakone volcano are as follows:

GROUNDMASS PYROXENES

Rock No. 1. $2V=0^{\circ}$ to very small angles. Rock No. 2. Pyroxene not reported. Rock No. 3. $\begin{cases} Type \ 1 \ 2V \doteq 43^{\circ} \\ Type \ 2 \ 2V \doteq 0^{\circ} \end{cases}$ nearly equal amounts of 1 and 2. Rock No. 4. $\begin{cases} 2V=43^{\circ}, 39^{\circ} \\ 2V=29^{\circ} \end{cases}$ observations on three random grains. Some nearly uniaxial grains also present. Rock No. 5. Augite $2V=46^{\circ}$, and a little nearly uniaxial pigeonite present. Rock No. 6. $\begin{cases} Type \ 1 \ 2V=49^{\circ}-42^{\circ} \\ Type \ 2 \ 2V \doteq 0^{\circ} \end{cases}$

ZONED PHENOCRYSTS

Rock No. 1. Augite $2V=49^{\circ}-46^{\circ}$. Rock No. 2. Augite $2V=52^{\circ}-48^{\circ}$ core; 41° margin. Rock No. 3. Augite $2V=50^{\circ}-48^{\circ}$ core; 42° margin. Rock No. 4. Augite $2V=51^{\circ}-49^{\circ}$ core; 39° margin.

	core		margin	
crystal a	2V	49°	39°	
crystal b	2V	49°	44°	
crystal c	2V	51°	42°	
crystal d	2V	51°	0	
crystal e	2V	50°		
crystal f	2V	49°		

¹¹ The augite of this paper.

Rock No. 5. (1) Pigeonite $2V = 17^{\circ} - 10^{\circ}$ core, sharply defined marginal zone $2V = 48^{\circ}$.

$\begin{array}{c} \mbox{crystal} \ a \\ \mbox{crystal} \ b \\ \mbox{crystal} \ c \\ \mbox{crystal} \ c \\ \mbox{crystal} \ d \\ \mbox{crystal} \ d \\ \mbox{crystal} \ e \end{array} = \begin{array}{c} 2 V = 10^{\circ} \\ 2 V = 12^{\circ} \\ 2 V = 16^{\circ} \\ 2 V = 17^{\circ} \\ 2 V = 13^{\circ} \end{array}$	$2V = 47^{\circ}$ $2V = 49^{\circ}$ $2V ca45^{\circ}$ $2V ca45^{\circ}$

(2) Augite $2V = 48^{\circ} - 43^{\circ}$ core; $2V = 47^{\circ} - 43^{\circ}$ margin,

	core	margin
crystal <i>a</i> crystal <i>b</i> crystal <i>c</i> crystal <i>d</i>	$2V = 45^{\circ} 2V = 45^{\circ} 2V = 44^{\circ} 2V = 47^{\circ}$	47° 44° 43° 44°

Rock No. 6. Pigeonite $2V \doteq 0^{\circ}$.

Augite $2V = 47^{\circ}$ core, $2V = 46^{\circ}$ margin.

Kuno (1940) groundmass pyroxenes, Hakone volcano.

Type (1) $2V = 44^{\circ} - 36^{\circ}$.

Type (2) $2V \doteq 0^{\circ}$.

In the above observations it can be noted that no optic angle values between $2V=29^{\circ}$ and $2V=36^{\circ}$ are given. Furthermore, excluding one measurement of $2V=36^{\circ}$ and one measurement of $2V=29^{\circ}$, there are then no values between $2V=17^{\circ}$ and $2V=39^{\circ}$. Thus out of forty-six specific observations thirty-four fall between 52° and 39° and ten between 17° and 0° .

In the following twelve papers two clinopyroxenes (excluding phenocrysts) are present in the rocks described and are clearly so recognized by the authors.

(1) Cohen (1887) found two clinopyroxenes in a diabase from Richmond, Cape Colony. The following optic angle values are reported (converted by present writer from 2E to 2V) $8_4^{1\circ}$, 10° , 12° , 13_2° , 15° , $18_2^{1\circ}$, and for a second pyroxene $44_2^{1\circ}$.

(2) Hovey (1892) examined a diabase near Rio de Janeiro, reporting two clinopyroxenes, the optic angle for one $2V = 21\frac{1}{2}^{\circ}$ and 19°, and for the other $46\frac{1}{2}^{\circ}$.

(3) Hovey also describes two clinopyroxenes in the Halleberg diabase, Sweden, and gives the optic angle for one, $2V=21^{\circ}$.

(4) Backlund (1907)* found two clinopyroxenes in the same diabase, for one $2V = 15\frac{1}{2}^{\circ} \perp$ to (010), and for the other $2V = 57^{\circ}$ or less parallel to (010).

(5) Pirsson (1898) writes of two clinopyroxenes, previously analyzed by Hawes, in the West Rock, New Haven, diabase. Optic angle measurements on these pyroxenes by the

* Since compiling these data the writer finds that Backlund described two clinopyroxenes in a large number of diabases from Spitzbergen, King Charles, Land, and Xiririca (Brazil), Halle-Hunneberg and Köpalla (Sweden), and Anabar (Siberia). writer gave for one $2V = 44\frac{1}{2}^{\circ}$, 48°, 49°, and several near 45°, and for the other $2V = 22^{\circ}$, 21°, 20°, 15°, 14°, $12\frac{1}{2}^{\circ}$, and a number between 10°–0°, optic plane perpendicular to (010).

(6) Wahl (1907) notes two clinopyroxenes in several diabases, that at Pierri-Perävaara, Karelia, gave $2V=38\frac{1}{2}^{\circ}$ for one and $2V=18^{\circ}$ for the other (as converted from 2E by the writer).

(7) Asklund (1925) found a little clinopyroxene with an optic angle near 0° surrounding hypersthene, and a second clinopyroxene described as diallage-like augite in a noritic gabbro from Stavsjö, Sweden.

(8) Gillson (1926) notes two clinopyroxenes in the Westfield, Massachusetts, diabase. Two optical angle measurements on one of these gave $2V = 10^{\circ}54'$ and $24^{\circ}16'$. The other has a 2V about 60° (evidently not measured).

(9) Holmes and Harwood (1928) find two clinopyroxenes in many of the Whin Sill rocks, one of these, the dominant pyroxene, has an optic angle near 50° and the other is in all cases near 0° .

(10) Tyrrell and Sandford (1934) note a purplish brown augite and a colorless clinopyroxene which is virtually uniaxial in gabbroic rocks from Spitzbergen.

(11) Bugge (1940) describes a pigeonite with $2V=16^{\circ}$, optic plane parallel to (010), and an augite with $2V=52^{\circ}$ in a hyperite from the Arendal district of Norway.

(12) Walker (1940) writes of pigeonite and augite in a number of specimens from the Palisades diabase. Measurements in one such specimen by the present writer gave for one pyroxene $2V = 42^{\circ}$, 43° , 44° , 44° , 46° , 47° , 48° , and 49° , and for the other $2V = 12^{\circ}$, 15° , 17° , 22° and 23° , optic plane perpendicular to (010).

In two other papers there can be no doubt of the presence of two clinopyroxenes from the descriptions given but the authors do not specifically so state. Benson (1916) makes the following comment with regard to the clinopyroxenes of an Antarctic dolerite: "In the same slide crystals may occur the optic angles of which vary from 90° to 0° (2E). The most frequent values are those lying between 0° and 30° and from 65° to 90°." (Estimated 2Vs by the writer 38° to 50° and 0° to 17°.) Bogue and Hodge (1940) examined Cascade andesites from Oregon and found that the groundmass pyroxenes were "pigeonites," but the optic angle values as recorded on a graph are as follows: $2V=49^{\circ}$, 49° , 48° , 48° , 45° , 44° , 43° , 42° , 42° , 40° , 40° , 36° , 35° , and $2V=26^{\circ}$, 22° , and 20° .

The optic angle measurements above can be considered a fairly representative random sample. If all of these be plotted on a frequency of occurrence curve as Fig. 2A, the gap in values is evident. Even if the gap were not present on this curve (as a result perhaps of both the effect of minor constituents and small observational errors), the two well marked peaks on the curve would cast doubt on the assumption that a complete series of clinopyroxenes from augite to pigeonite exists. The two peaks suggest the presence of two distinct solid phases each of which is somewhat variable in composition. Considering those optic angles of pigeonites which lie in the plane \perp to (010), the gap becomes even more evident since they should be regarded as being less than 0° (Fig. 2B). The orientation of the optic plane was disregarded in making the upper diagram (Fig. 2A) since this orientation is not given in many of the papers cited. Almost all of the pigeonites examined by the writer have their optic plane perpendicular to (010).

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A detailed discussion of zoned relations of clinopyroxenes in some of the above rocks would lead to similar conclusions. Crystals having augite cores $(2V = \pm 45^{\circ})$ and pigeonite borders $(2V = \pm 0^{\circ})$ are commonly pointed to as indications of a complete series of solid solutions. In all cases examined by the writer and in accurate descriptions in the literature there is a sharp boundary between the augite and pigeonite of these crystals and a gap in optic angle values, just as found in the analysis of the previous paragraphs. It may be mentioned that, though less com-



FIG. 2. (A and B)

mon, pigeonites with augite borders are also found. The comparative rarity of the latter might be ascribed to the fact that the majority of normal mafic magmas lie in the field which crystallizes augite first (on the augite side of Tsuboi's two pyroxene boundary).

In each of the occurrences described above pigeonite was accompanied by augite. In all rocks examined by the writer this was also true. Several cases were noted in the literature in which pigeonite was said to be present in the rock, but augite was not specifically mentioned as accompanying it. These are the chemically analyzed specimens from Pigeon Point, mentioned by Winchell (1900), Washington's Deccan trap pyroxene, Doelter's (1882) Cape Verde Island groundmass pyroxene, and the Fölgö and Onega pigeonites of Wahl (1907). In all of these cases, however, the analyses themselves suggest a mixture of augite plus pigeonite (see discussion of chemical composition of pigeonite). Thus two general conclusions may be drawn from the above discussion of pigeonite.

Conclusion 1. Limited, not complete, solid solution is the rule for natural clinopyroxenes intermediate between the diopside-hedenbergite series and the clinoenstatite-clinoferrosilite series for a large part of the whole composition field enclosed by the above end-members.

Conclusion 2. Pigeonite is accompanied by augite in most if not all natural occurrences. An exceptional case might be postulated where pigeonite was the first of the two clinopyroxenes to crystallize and the magma was completely solidified (as for example by chilling to a glass) before the second clinopyroxene, augite, appeared.

Pyroxenes of Diabases and Dolerites

The most ideal rock types in which to investigate pyroxenes and pyroxene relations of mafic magmas are the diabases and dolerites. The groundmass of basalts is, as a rule, difficult to study because of the small grain size and the phenocrysts are commonly of abnormal composition, as will be shown later in the discussion. Other disadvantages inherent in the study of effusives are the complexities resulting from non-equilibrium conditions caused both by rapid chilling at the surface and by rapid rises in temperature produced by oxidation. With due regard for these complexities it can be shown that crystallization of basalt follows the same pattern as for intrusive diabase and dolerite, with minor modifications in one direction or another resulting from a rapidly varying environment and imperfect equilibrium conditions. In the coarser grained, more slowly cooled gabbroic or noritic intrusions the course of pyroxene crystallization is the same as in diabase and dolerite, but because of almost perfect equilibrium conditions certain less stable, transitional, phases are completely absent in the final rock products, thus making them less easily susceptible to interpretation.

A. Triassic Diabases of New Jersey

The first pyroxene to separate from the Palisades-Rocky Hill Sill and the sill south of Lambertville appears to be a normal augite $(2V=45^{\circ}\pm 5^{\circ})$. It occurs in the chilled border facies as glomero-porphyritic aggregates of microphenocrysts. A little olivine accompanies or may slightly precede it. The groundmass contains pigeonite and augite, with pigeonite in excess. Immediately above the lower chilled border facies at Lambertville and in the Palisades, hypersthene appears as fairly large ophitic crystals, accompanied by augite. About twenty per cent of olivine is present in this zone in the Palisades—the well-known olivine layer—

and less olivine is present at Lambertville. At Rocky Hill this development of a marked melanocratic layer has not been observed. It may be noted that the hypersthene is of the clear, slightly pleochroic variety with no exsolution lamellae. Proceeding upwards in these sills the olivine disappears and both pyroxenes become more iron-rich (indices of refraction increase). The first evident change to be noted is the appearance of hypersthene with rather irregular oriented plates or rows of globules of exsolved augite. The change takes place when the hypersthene reaches a MgO: FeO molecular ratio of approximately 7:3. All hypersthenes more iron-rich than this 7:3 ratio exhibit the roughly oriented inclusions. In specimens taken from the level at which the change occurs individual crystals may be seen with cores of clear hypersthene and border zones of slightly more iron-rich hypersthene containing the inclusions. At a higher level in the Palisades sill, orthopyroxene disappears entirely, but its place is evidently taken by pigeonite $(2V=0^{\circ}-25^{\circ})$, optic plane \perp to (010)). The augite continues to crystallize as before. At this level the rock resembles the West Rock, New Haven, occurrence described by Pirsson (1898), except that both the augite and pigeonite have a faintly brownish color. In the West Rock occurrence the pigeonite is colorless and has a characteristic type of alteration so that the two clinopyroxenes are easily distinguished, but in the Palisades they can only be distinguished by the differences in their optic angles (see measurements on a previous page). In the most iron-rich differentiates of the New Jersey diabases, pigeonite disappears and only ferroaugite remains. Phillips' (1899) two analyses of clinopyroxenes from the Rocky Hill diabase were both taken from such late ferriferous differentiates.

The augites, though free of exsolution lamellae in the more quickly cooled facies, commonly exhibit exsolved hypersthene as lamellae parallel to (100) in the more magnesian varieties, and parallel to (001) in the more ferriferous. They also show in some cases an alteration which appears to be identical with that described by Krokström (1932, p. 279) for the Breven dolerite.

B. Karroo Dolerite, Downes Mountain

A Karroo Sill has recently been described in some detail by Walker and Poldervaat (1941). The pyroxene relations are remarkably similar to those described for the New Jersey Triassic diabases with one notable exception, namely, that orthopyroxene is the first pyroxene to crystallize rather than augite.

The crystallization sequence of the pyroxenes is summarized below:

1. Earliest pyroxene, orthorhombic, bronzite En_{83} , followed after a short interval by augite.

2. More iron-rich, hypersthene with oriented plates of augite which is accompanied by augite.

3. In the upper part of the sill the place of orthopyroxene is taken by pigeonite $2V=0^{\circ}-12^{\circ}$; augite is still present. (An "antipathic relationship" of orthopyroxene to pigeonite is pointed out.)

4. The late stage pyroxene mentioned is called a "hypersthene augite" which appears to be the ferroaugite of this paper (or an augite very near the ferroaugite boundary). From the optic angle values given it seems probable that a little pigeonite is also present, but that the ferroaugite and the pigeonite are so similar that no distinction was made between the two $(2V=20^{\circ}-45^{\circ})$.

5. In the final stage of crystallization a pegmatitic facies was developed which contains a much altered clinopyroxene. From the description given and by analogy with the Palisades diabase, this is a ferroaugite.

Certain interesting relationships are observed on individual pyroxene crystals. Pigeonites are described which have a shell of augite surrounding them in optical continuity. The boundary between the two phases is distinct and sharp. Optical angle measurements on several such grains are given as follows:

Core $2V = 0^{\circ}$, 0° , 3° , 5° , 11° , 12° , 12° (=pigeonite).

Shell $2V = 43^{\circ}$, 40° , 39° , 38, $^{\circ}34^{\circ}$, 34° , 31° (=augite).

A gap in values between 31° and 12° may be noted. Aside from one augite with an optic angle value of 31° , all readings fall within the optic angle ranges for augite and pigeonite as given in this paper. As suggested previously the 31° value (which is 1° lower than the division point given) may be the result of the presence of some minor constituent in more than normal amount, or may be due to a small observational error.

It is also interesting to note that in this sill (where orthopyroxene has been demonstrated to have crystallized first) pigeonite crystals have a shell of augite around them, rather than the reverse relationship which is so common in those magmas which have crystallized augite first.

Cases are also noted where augite formed a shell around the hypersthene which contains oriented plates of augite, the hypersthene being present instead of the pigeonite as described above.

From the index of refraction values given by Walker and Poldervaat it appears that the change from normal orthopyroxene to orthopyroxene with oriented plates of augite took place at a MgO:FeO molecular ratio of 73:27 (\pm 3), which is consistent with the values found in a number of other mafic intrusives.

C. Whin Sill and Related Dikes

From Teall (1884) and the more recent study of Holmes and Harwood

(1928), the pyroxene relations in this suite of mafic intrusives can be worked out. The same phases appear to be present as were described in the New Jersey diabases.

The following pyroxenes are described by Holmes and Harwood:

(1) Hypersthene

- (2) Hypersthene with "strips" of monoclinic pyroxene
- (3) Pigeonite $2V \doteq 0^{\circ}$.
- (4) Augite $2V \doteq 50^{\circ}$. "The dominant pyroxene."

Holmes and Harwood state that: "we do not understand how it is that hypersthene is the dominant magnesian pyroxene (*in some rocks*) whereas in others its place is largely taken by A (*pigeonite*), but it is clear that the two are mutually complementary...." Hypersthene is conspicuous in the northern occurrences where pigeonite is lacking, and pigeonite is commonly present in the southern part of the area where hypersthene is absent. The analyzed rock 572, Grassless Burn, Elsdon, however, has three pyroxenes. A little hypersthene is enclosed in nearly uniaxial augite (*pigeonite*), and ordinary augite is also present. In the more ferriferous facies, such as in Teall's Chaldron Snout, "coarse veins," analyzed specimen, and in the Tyne Head analyzed specimen only one pyroxene is present: augite or ferroaugite.

There is a slight suggestion in Holmes' description that the hypersthene starts to crystallize ahead of the augite, but this point is not at all clear. The normative molecular ratio of Wo:En:Fs is such, that it appears to lie very close to, or just above (on the augite side of) the two pyroxene boundary. In all other respects, if not in this respect, the crystallization of the Whin Sill pyroxenes is the same as in the Triassic diabases.

D. Diabasic Border Facies of the Stillwater Complex.

The fine grained border facies of the Stillwater Complex has a subophitic texture with hypersthene greatly in excess of augite. The hypersthene is relatively iron-rich (MgO: FeO = 56:44), and it contains roughly oriented inclusions of augite as plates. The textural relations indicate crystallization of the lime-poor pyroxene* first, followed by crystallization of both lime-poor pyroxene and augite together.

Igneous rocks of basaltic composition which show crystallization of lime-poor pyroxene before augite are exceedingly rare. It seems likely that in most cases olivine will crystallize in such rocks rather than a lime-poor pyroxene. In magmas of less mafic composition (andesitic) the crystallization of a lime-poor pyroxene first, in place of augite, is fairly

* Lime poor pyroxene = pigeonite or orthopyroxene.

common. The majority of the Japanese andesitic magma products show a lime-poor pyroxene crystallizing before augite and many of the Lesser Antilles magmas have the same characteristic.

E. Summary of Pyroxene Relations in Diabases and Dolerites.

1. Augite normally crystallizes first, but in rare cases a lime-poor pyroxene may separate ahead of the augite.

2. Shortly after the appearance of the first pyroxene it is joined by the second, and the two crystallize together for the greater part of the crystallization history of the intrusive.

3. Hypersthene changes abruptly to hypersthene with oriented plates or rows of globules after a certain MgO:FeO molecular ratio is reached (near 70:30).

4. Hypersthene with oriented inclusions gives way to pigeonite as the crystals become still more iron-rich, pigeonite and augite separating simultaneously during this portion of the crystallization history.

5. Pigeonite ceases to crystallize after reaching a MgO:FeO ratio near 35:65 and ferroaugite continues alone.

Pyroxenes of Coarse Grained Mafic Intrusives, Norites and Gabbros

A. Stillwater Complex, Montana

In this sheet-like complex the writer has collected a series of specimens from the floor upwards, and inasmuch as this intrusive has been built up by settling of crystals layer upon layer, it is possible to study not only the relations of the pyroxenes to each other and to plagioclase in individual specimens, but also to observe changes which occur as crystallization proceeds.

The first ferromagnesian mineral to appear in the course of crystallization of the Stillwater magma is a magnesian olivine. It is soon followed and its place taken by an orthopyroxene, bronzite, with a MgO:FeO molecular ratio of approximately 86:14. As crystallization proceeds the MgO:FeO ratio gradually decreases. These orthopyroxenes contain roughly five molecular per cent of Wo component which exsolves from them in fine diopsidic lamellae parallel to (100) with slow cooling, as described by the present writer and Phillips (1938 and 1940). Associated with the earliest orthopyroxene rocks is a bright green chrome-endiopside, found in small amounts. It is completely interstitial to the bronzite and evidently crystallized from the liquid between the settled euhedral crystals of bronzite.

With continued crystallization the clinopyroxene changes in color from bright green to the normal dark green of augite. It is still present in very small amounts. After the orthopyroxene reaches a MgO: FeO molecular ratio of 80:20, abundant clinopyroxene appears as settled crystals separating contemporaneously with hypersthene. The two pyroxenes continue to crystallize simultaneously from this level in the complex upwards to the highest exposure. The uppermost portion of the complex is covered so the crystallization cannot be traced to completion.



FIG. 3. Oriented plates of augite in a hypersthene from the Stillwater complex.

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FIG. 4. Hypersthene with oriented plates of augite in the Palisades diabase. Arrangement less regular than in Fig. 3.

Where the hypersthene reaches a MgO: FeO ratio of approximately 73:27, an abrupt change takes place in it. In composition this change consists in an increase of the Wo component from five molecular per cent to nine per cent. In thin section it is evident because this orthopyroxene has plates of diopsidic clinopyroxene commonly oriented approximately parallel to what appear to be dome planes in the orthopyroxene. The fine lamellae parallel to (100) are also developed. They are offset on crossing the oriented plates in such a manner that it appears that they are younger than the plates (Fig. 3).

PYROXENES OF MAFIC MAGMAS

B. Bushveld Complex. Transvaal

The pyroxenes of the Bushveld Complex are almost identical with those described above for the Stillwater. The course of crystallization is the same and the hypersthene undergoes the same abrupt change to the variety with oriented plates at or near a MgO:FeO molecular ratio of 73:27.

C. Skaergaard Intrusion, East Greenland

The lower portion of this intrusive described by Wager and Deer (1939) is hidden so that little is known of the earlier ferromagnesian phases. The lowest exposed horizons have two pyroxenes practically identical in composition with the two pyroxenes of the uppermost exposed horizon of the Stillwater. A "border group" picrite gives some indication of the type of rock to be found in the deeper hidden portion. This rock contains an augite and a bronzite, approximately En₈₀, which shows the fine lamellae parallel to (100) as do the Stillwater and Bushveld orthopyroxenes of that composition. The next most magnesian orthopyroxene described is near Enfo and has the oriented plates also found in all the Bushveld and Stillwater orthopyroxenes with less magnesia than En₇₃. The change from the first type to the second must therefore take place between Enso and Enso, but cannot be more precisely determined from the data given. Orthopyroxenes with oriented plates continue to be present together with augite until a composition of near En₃₅ is reached. Beyond this, orthopyroxene is absent, but ferroaugite and iron-rich olivine continue to crystallize. Olivine is found through most of the exposed section of the Skaergaard, the magma being undersaturated whereas the Bushveld and Stillwater are just about saturated having neither appreciable normative olivine nor quartz.

The clinopyroxenes are most interesting in this intrusion because they range all the way from fairly magnesian augites to ferroaugites with practically no magnesia. The ferroaugites are deficient in the Wo component compared to common augites.

Table 2 (In Part 2) shows the progressive changes in pyroxenes of the Stillwater and Skaergaard intrusions as crystallization proceeds.

D. Duluth Gabbro, Minnesota

The writer has relatively less information on the pyroxenes of this intrusion. The data presented are based on a suite of some forty specimens most of which were collected by Edward Sampson in 1932.

A purplish augite is the first pyroxene to separate from the Duluth gabbro. It occurs as coarse poikilitic crystals including olivine in the peridotite near the base of the lopolith. Higher in the intrusion hypersthene appears, but it is in all cases subordinate in amount to the augite. As in the Stillwater, Skaergaard, and Bushveld it gives way to hypersthene with oriented plates as the orthopyroxene becomes more ferriferous.

Some of the specimens of this suite contain only augite or ferroaugite, and presumably hypersthene with oriented plates ceases to crystallize as in the Skaergaard intrusion. The writer is not positive that this is the case, however, since the particular specimens examined show small areas of strongly pleochroic chlorite which could possibly represent completely replaced hypersthene.

E. Summary of Pyroxene Relations in Coarse Grained Mafic Intrusives.

1. Either augite or bronzite begin to crystallize first; examples of the latter type are exceedingly rare.

2. Shortly after the first pyroxene appears, the second begins to crystallize with it.

3. If the first pyroxene is bronzite the earliest clinopyroxene is chromeendiopside.

4. After the MgO:FeO ratio of the orthopyroxene reaches approximately 73:27, hypersthene gives way to hypersthene with oriented plates of augite.

5. Augite and hypersthene with oriented plates continue to crystallize together until a MgO: FeO ratio near 35:65 is reached.

6. Hypersthene then drops out and ferroaugite continues to crystallize until an almost pure Ca-Fe ferroaugite is reached in the final stage.

7. As compared with the fine grained intrusives the relatively longer range of crystallization of hypersthene with oriented plates may be noted, and the complementary absence of pigeonite. This is the only essential difference between the coarse grained gabbros and norites and the fine grained diabases and dolerites.

Pyroxene Relations in Effusive Rocks, Basalts and Andesites

In the effusive rocks it is much more difficult to work out pyroxene relations, because of the small grain size of the groundmass, abnormal compositions of many phenocrysts, and the lack of differentiation exhibited by flows. It is necessary to choose favorable specimens from many parts of the world in order to get at the particular features required for an understanding of the relations. The writer is, therefore, dependent to a much larger extent on the literature supplemented by only a few personal observations.

A. Phenocrysts.

A clinopyroxene, augite or diopside, and an orthopyroxene, hypersthene, are the common pyroxene phenocrysts of mafic lavas. Either one, or, less commonly, both may be present. The hypersthene does not contain the fine exsolution lamellae parallel to (100). Hypersthene with oriented plates is not found. Pigeonite as phenocrysts is exceptionally rare (Mull and Hakone) and is limited to lavas with a low MgO: FeO ratio, as a rule (andesites). It is significant, however, that it does occur in this form.

Though in some lavas the clinopyroxene phenocrysts are comparable to the augite crystals found in diabases, gabbros, etc., it is more common to find clinopyroxenes of a diopsidic, rather than augitic composition (the Wo:En+Fs ratio is near 50:50 rather than 40:60). There are no equivalent diopsidic clinopyroxenes in the common mafic intrusives. The conclusion is that the clinopyroxene phenocrysts were normal augites in the intratelluric stage, but have for some reason been changed in composition upon approaching the surface, or after extrusion.

The change which takes place can be noted by comparing the many analyses of phenocrysts in extrusives with normal augites of moderatedepth hypabyssal to plutonic intrusives. The change is readily recognized optically by the increase in the optic angle of the clinopyroxene as the composition changes from the normal composition Wo_{40} (En, Fs)₆₀, $2V = 47^{\circ} \pm toward Wo_{50}$ (En, Fs)₅₀, $2V = 60^{\circ} \pm$.

It may also be noted that the groundmass augite of extrusives either does not take part in this change or does so to a lesser extent.

A few observations are given below to illustrate the statements made above:

1. Barth (1931) gives the compositions of phenocrysts of Pacific lavas. All of these lie near the diopside-hedenbergite line.

2. Bogue and Hodge (1940) state that optic angles for phenocrysts of Cascade lavas range from $52^{\circ}-58^{\circ}$, plus one observation of an angle of 62°. Groundmass augites in the same rocks have optic angles averaging about $2V = 43^{\circ}$.

3. Examination of Triassic Watchung basalts by the writer shows that augite microphenocrysts have optic angles near $2V = 52^{\circ}$, whereas the groundmass augites average 3° less, and the augites of the Triassic intrusive sills average 2° less than the latter.

4. A dike extending upwards into an extrusive breccia was studied by R. Hutchinson (senior thesis, Princeton University 1941). Examination of augites in the dike some 600 feet below the original surface give values for the optic angle averaging $55\frac{1}{2}^{\circ}$, whereas those in the extrusive facies are $2\frac{1}{2}^{\circ}$ higher.

Considerably more investigation of augites of very near surface intrusives and extrusives will be necessary to arrive at a definite conclusion as to the nature and cause of this change. It is mentioned in this report mainly to emphasize that such clinopyroxenes are abnormal in that they lie off the main trend of crystallization of augites under moderate hypabyssal to plutonic conditions. A number of chemical analyses of "augites" from mafic lavas were made by Washington. All of these are close enough to Wo: En+Fs=50:50 to be classed as diopsides or salites. None of them would be called "augite" as defined in this paper. Most of them have a relatively high Al_2O_3 content and a slighly more than average amount of Fe_2O_3 as compared to augites of plutonic to moderately deep hypabyssal intrusives.

At present it is difficult to account for the abnormal character of these phenocrysts. It may have something to do with oxidation occurring near or at the surface and the accompanying increase of temperature, or it may be related to low pressure, or to the action of volatiles.

B. Groundmass.

The normal groundmass pyroxenes of mafic effusives are augite and pigeonite. In the highly ferriferous extrusives ferroaugite occurs alone. The appearance of hypersthene in the groundmass in place of pigeonite is exceedingly rare, the reverse of the relations as regards the phenocrysts.

C. Summary of Pyroxene Relations in Mafic Effusives.

- (1) (a) Phenocrysts i. Augite or diopside alone.
 - ii. Augite or diopside+hypersthene.
 - iii. Hypersthene alone.
 - iv. Very rare-pigeonite in place of hypersthene in ii and iii above.
 - (b) Groundmass i. Augite+pigeonite.
 - ii. Ferroaugite alone.
 - iii. Very rare hypersthene in place of pigeonite in i above.

(2) Hypersthene with oriented plates (or more irregular oriented inclusions) of augite is not present in extrusives,¹² but the complementary mineral, pigeonite, is common. This is the exact reverse of relations in the coarse grained intrusives where pigeonite was never present, but hypersthene with oriented plates is common. The fine grained intrusives are intermediate between the coarse grained intrusives and the effusives in that either pigeonite or hypersthene with oriented plates may be present.

¹² One exception apparently noted by Kuno (1938).

(3) Intratelluric augite phenocrysts in many cases change towards diopside in composition during extrusion. Account must be taken of this in establishing the course of crystallization of clinopyroxenes from mafic magmas.

(4) Excluding this minor change in composition of augite phenocrysts towards diopside, the chemical composition of the pyroxene phases and the change in composition with differentiation is the same in coarsegrained intrusives, fine-grained intrusives and effusives of common mafic magmas.¹³

(To be continued)

¹³ Chemical equivalence of pigeonite and hypersthene with oriented plates is shown later in this paper.