PYROXENES OF COMMON MAFIC MAGMAS. PART 2.

H. H. HESS, *Princeton University, Princeton, New Jersey.**

TABLE OF CONTENTS OF PART 2

HYPOTHESES ON THE TREND OF CRYSTALLIZATION
OF PYROXENES IN BASALTS

The writer has extracted and herewith presents what he considers to be the kernel of thought in each of several papers dealing with the crystallization of pyroxenes from basalts. Many of the concepts in these papers are built upon primary data presented in Wahl's classic paper (1907) "Die Enstatitaugite" and various general papers by J. H. L. Vogt. A number of other less fundamental articles dealing with pyroxenes in basalts might have been included but those quoted seemed sufficient to give the trend of ideas on the problem at hand.

Asklund (1925)

Asklund calculated the MgO-CaO-FeO proportions of all superior analyses of diabases, gabbros, norites and pyroxenites in Washington's Tables. By referring to the original articles on these rocks he noted, whenever possible, whether one or two pyroxenes were present in the rock.

Upon plotting the points for rocks with one and two pyroxenes he found an area in which two pyroxenes were characteristic and outside of which only one pyroxene was the rule (Fig. 5). From this he concluded that despite the suggestion from Bowen's laboratory investigation of clinoenstatite-diopside relations, (which showed complete solid solution with a minimum), natural occurrences indicated limited miscibility between calcium-poor and calcium-rich magnesian pyroxenes. This is the major contribution of the paper. There follows a considerable discussion of the
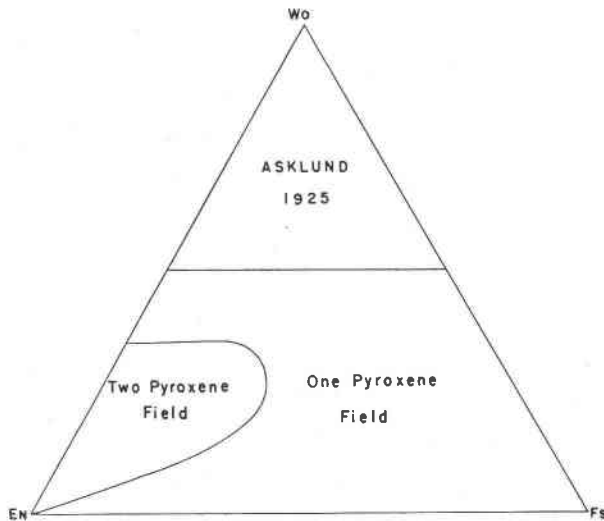

FIG. 5

chemistry of crystallization of pyroxenes. In the present writer's opinion this is of little value since it is based on certain unacceptable tacit assumptions, the most important of which is that only the chemical composition of the rock is considered and not the probable magma from which the rock was derived. Nevertheless, the paper is of much importance since it marks the first step in the trend of thought to be followed by many subsequent papers and no doubt formed a basis for further exploration and served as a stimulus towards this end.

Barth (1931)

Barth studied pyroxenes from basalts and took exception to Asklund's conclusion of partial miscibility of pyroxenes. The following quotation sums up Barth's conclusions: "Pigeonite is the most abundant pyroxene of 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 (see Fig. 6). . . . In agreement with the experimental studies of Bowen the present survey indicates a complete series of solid solutions in natural basaltic pyroxenes and consequently fails to demonstrate the discontinuity proposed by Asklund." Barth points out many fundamental details in pyroxene relations in the paper and has an ingenious method of attack on the problem which to some extent is followed by all later investigators.
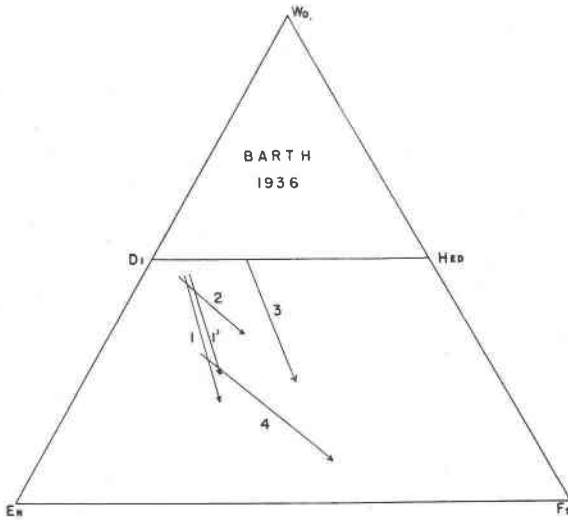
Fig. 6

His deduction as to the chemical composition of the groundmass pyroxene based on the normative Wo-En-Fs of the rock is open to question in that it assumes only one pyroxene is present.

Barth's views in a later paper (1936) are essentially the same, but stated even more forcibly. ". . . literally hundreds of typical basalts from all over the world show with remarkable uniformity the progressive change in the pyroxene phases from diposidic to clinohypersthenic, none but a very determined doubter could therefore fail to accept this as the *normal* course of crystallization of pyroxene from a basaltic lava."

Tsuboi (1932)

Tsuboi's skillful analysis of the trends of crystallization of pyroxenes from magmas, with particular examples from Japanese volcanic suites, shows that the views of Asklund and Barth are not incompatible, and

goes more deeply into the chemical relations. The following quotation and Fig. 7 sum up his conclusions.

"In the intratelluric stage, either one of the monoclinic and rhombic pyroxenes starts the crystallization according to whether the composition of the original magma is in the field of monoclinic or of rhombic pyroxenes. As crystallization proceeds, the residual liquid changes its composition, following a course such as that indicated either by L_1 or by L_1'; and when the two-pyroxene boundary, CD, is reached the other one of the two
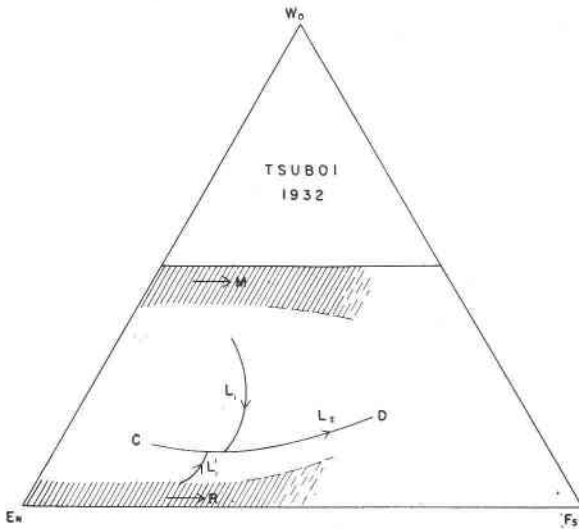
Fɪɢ. 7

pyroxenes joins in the crystallization. In the meantime the crystals of monoclinic and rhombic pyroxenes change their compositions respectively from diopsidic to hedenbergitic, and from enstatitic to hypersthenic, approximately as indicated by the arrows M and R. The hatched areas in the figure represent roughly the limits of miscibility of the pyroxenic components under the condition (designated as "condition A") that prevails in the intratelluric stage.

"In the effusive stage, as the great majority of instances shows, another condition (designated as "condition B") prevails, under which there is no limit to the miscibility of the pyroxenes. Then the pyroxenic components of the residual liquid crystallize in a single pigeonitic phase, without splitting into two pyroxenes. In exceptional cases, however, condition A seems to prevail even in the effusive stage.

"The outstanding feature of my theory is in the assumptions that (i) the pyroxenic components are only partially miscible in the intratelluric stage, while (ii) they are completely miscible in the effusive stage (with rare exceptions)."

Kuno (1936)

The writer considers Kuno's papers to be among the finest examples in the literature of careful, accurate, and intelligent petrographic work. It is because of this quality that Kuno is able to make an important addition to Tsuboi's general theory of trends of pyroxene crystallization.

Kuno observes pigeonite phenocrysts in the lavas of the Hakone volcano and concludes that they must represent a stable phase under certain conditions in the intratelluric stage.

In general Kuno follows Tsuboi, but adds that if in the intratelluric stage the Mg:Fe molecular ratio is less than 45:55, one pyroxene (pigeonite) becomes a stable phase. Where the ratio exceeds 45:55 a two-pyroxene field (augite and orthopyroxene) exists as Tsuboi stated. In the effusive stage Kuno believes that pigeonite will form metastably because of rapid crystallization as suggested by Bowen and Schairer, regardless of whether the composition is in the two pyroxene field or the pigeonite field.

Wager and Deer (1939)

Wager and Deer in a magnificent memoir on the Skaergaard intrusion, made a thorough investigation of the clinopyroxenes, including a number of chemical analyses. It was thus possible to extend the curve for crystallization of the clinopyroxene of basaltic magmas from the early stages, as given by Kuno and Kennedy, to the very latest stage with extreme differentiation; at which stage they are practically pure Ca-Fe pyroxenes (Fig. 8). A study of the orthopyroxenes shows that they accompany the clinopyroxene up to that point where the Mg:Fe molecular ratio becomes approximately 35:65 They thus shift Kuno's limit for the intratelluric two-pyroxene field 10 per cent farther towards the iron-rich side of the diagram.

In the present paper the iron-rich clinopyroxenes of the Skaergaard would be called *ferroaugites*. Wager and Deer following more or less accepted usage called them *pigeonites*. To do so, however, completely confuses the genetic relations between the pyroxenes as was shown elsewhere in this paper. These ferroaugites are not the same phase as the typical pigeonites of the groundmass of basalts with 2V near 0°. Thus Wager's and Deer's discussion of the trend of crystallization of the pyroxenes, based on this unacceptable assumption, is considered invalid. This is not meant to be an unfavorable reflection on the work of Wager and Deer,

for which the present writer has a very high regard. From the data they had, the conclusions they drew follow logically. It is rather a commentary on the confusion which may result from the lack of an adequate nomenclature for pyroxenes and the failure of the science as a whole to make
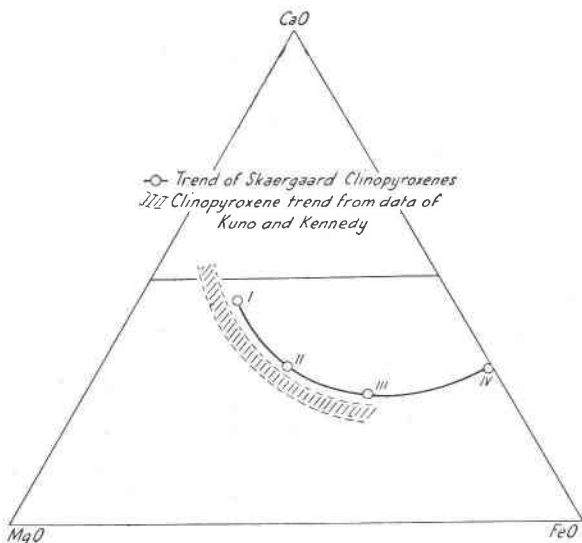

Fig. 8

precise distinctions between even the commonest varieties of clinopyroxenes.

Present Writer's Conclusion with Regard to Pyroxene Relations

Before proceeding to a theory as to the course of crystallization of pyroxenes from common mafic magmas, it is desirable to bring together in the form of conclusions, and to some extent speculations, various observations concerning pyroxene relations set forth in the descriptive portion of this paper.

Very few chemical analyses of pigeonites have been made and it appears to the writer that only one of these is completely satisfactory. This one is the so-called "uniaxial augite" from Mull (Hallimond 1914). An analysis of the pyroxene from a meteorite (eucrite, Moore County, North Carolina, Henderson and Davis, 1936) probably represents accurately the chemical composition of the pigeonite found in the specimen, but has the disadvantage that part of it has apparently broken down, invert-

ing to hypersthene with thin plates of augite. It is thought that this breakdown of the pigeonite would not involve any change in the bulk composition of the pyroxene. Bowen (1933) has estimated the composition of an iron-rich pigeonite from a slag.

TABLE 1

	1 Mull, Hallimond	2 N. C. Eucrite, Henderson and Davis	3 Bushveld, Hy inverted from Pigeonite	3a* Same as 3, subtract small amount impurity	4 Stillwater, Hy inverted from Pigeonite in hornfels	5 Slag, Bowen
SiO₂	49.72	49.37	51.67	51.40	50.24	
Al₂O₃	.90	1.55	1.80	1.78	4.52	
Fe₂O₃	1.72	1.83	1.40	1.40	.41	
FeO	27.77	26.44	20.57	20.68	21.81	
MgO	12.69	15.54	19.34	19.37	15.81	
CaO	3.80	4.60	4.45	4.07	4.39	
Na₂O	.23	—	.12	.11	.18	
K₂O	.12	—	—	—	.04	
H₂O+	1.27	—	.36	.37	1.42	
H₂O−	.08	—	.04	.04	.04	
TiO₂	.85	.62	.30	.30	.69	
MnO	.98	.37	.47	.48	.43	
Total Analyst	100.13 Hallimond	100.32 E. P. Henderson	100.52 R. B. Ellestad	100.00	99.98 R. B. Ellestad	
Molecular per cent {	Wo 9 En 40 Fs 51	9¾ 45¾ 44½		8½ 57 34½	10 50½ 39½	8¾ 12¼ 79

* Impurity, a small amount of augite (2.5%). The augite from this specimen was also analyzed so the correction should be quite accurate. The analysis was recalculated to 100 per cent.

Other purported analyses of pigeonites are as follows: (1) Pigeon Point (Winchell, 1900), (2) Åland Islands (Wahl, 1907), (3) Lake Onega (Wahl, 1907), (4) Deccan trap (Washington, quoted by Fenner, 1929), (5) Hiva Oa (Barth (1931A) and (6) Hakone volcano (Kuno 1940). In the writer's opinion all six of these analyses represent mixtures of augite and pigeon-

ite. Through the courtesy of F. F. Grout the writer obtained a thin section of the rock from which the analyzed "pigeonite" from Pigeon Point was separated. A. N. Winchell very kindly supplied the writer with some of the original pyroxene separate on which the analysis was made. Examination of the slide and pyroxene separate showed that purplish augite, $(2V = 43° - 47°, Z \wedge c = 40°)$ was present in considerable quantity in both. As pointed out previously pigeonite is always accompanied by augite in rocks. In specimens (2) to (6) the bulk pyroxene was analyzed and no attempt apparently was made to separate a pigeonite from an augite. In analyses (4), (5) and (6) a wide variation in optic angles was reported on the material analyzed, ranging from near 50° to 0°. This again, as previously pointed out, indicates that both augite and pigeonite are present. The material of analyses (2) and (3) are incompletely described and have the added disadvantage of being inferior analyses (summations over 101). In (6) Kuno notes many grains with $2V = 44° - 36°$ and another group with 2V near 0°.

In Table 1 the two analyses which the writer believes are representative of the mineral pigeonite are given and two analyses of hypersthene with augite plates, which the writer considers to be pigeonite inverted to orthopyroxene upon slow cooling. Note the uniformity of $CaSiO_3$ component shown in all of the analyses of Table 1.

A. Relation of Hypersthene with Oriented Plates to Pigeonite.

The mutually complementary relationship of hypersthene with oriented plates and pigeonite has already been discussed. Ordinary hypersthene of igneous rocks contains uniformly about four and a half molecular per cent of the Wo component in solid solution (probably as diopsidic pyroxene) (Hess and Phillips 1940). Hypersthene with oriented plates contains uniformly about nine per cent, or twice as much. This is the amount found in the reliable analyses of pigeonite (see Table 1). In the writer's opinion there is strong evidence to indicate that the hypersthene with oriented plates is pigeonite, which has by slow cooling inverted to orthopyroxene. The oriented plates represent the excess Wo above the four and a half per cent which is the maximum soluble in hypersthene and the excess separates from the orthopyroxene in the form of augite $(2V \doteq 50°)$. An additional indication of the inversion is the arrangement of the plates themselves. Hypersthene does not normally occur as twinned crystals in igneous rocks. Pigeonites commonly form either a pair or multiple twins with the composition plane (100). The oriented plates in many hypersthene crystals which contain them are arranged in two sets—herring bone-like—or in multiple sets in such a way as to suggest that each set was developed in a twin of the original pigeonite (see Figs. 3 and 4).

The commonest orientation of the plates is such that they are parallel to the *b* crystallographic axis and make an angle of approximately 74° with the *c* axis. This would be near a (102) plane in the hypersthene crystal, but a (102) crystal face has not been reported for this mineral and it seems to be an unlikely plane for development of lamellae by exsolution. If, however, the plane were related to the crystallographic directions of an original pigeonite, it would then become (001). Pigeonites commonly have a well developed (001) parting so that the orientation of the lamellae strongly suggests that they were developed in original pigeonite, before or during inversion to hypersthene. Exsolution lamellae having this orientation were observed in the pigeonite of the Moore County, North Carolina, eucrite (meterorite).

From the petrological evidence the case is also strong. Hypersthene with oriented plates is characteristic of *slowly cooled* intrusives and pigeonite is absent in these. Pigeonite is characteristic of *rapidly cooled* extrusives and hypersthene with oriented plates is absent in them. Whereas the intermediate type, the fine grained intrusives, may show both forms. In those rare cases where pigeonite began to crystallize in depth and the magma containing it was suddenly extruded, pigeonite phenocrysts will be found as in Hakone volcano.

B. *Relation of Hypersthene to Hypersthene with Oriented Plates.*

In the Stillwater, Bushveld, Skaergaard, and the New Jersey diabases it was shown that where the MgO:FeO molecular ratio of calcium-poor pyroxene was greater than approximately 7:3, normal orthopyroxene was present. When the ratio was less than 7:3, either hypersthene with oriented plates or pigeonite was present, depending probably on the rate of cooling. In the other igneous rocks discussed, such as the Duluth gabbro, Hakone andesites, Whin Sill, etc., the same relationship holds but the data were not available as to the exact ratio at which the change occurred. The immediate cause for this relationship can be found in Bowen's and Schairer's $MgO-FeO-SiO_2$ paper. A curve for the temperature of inversion of pyroxenes of the clinoenstatite-clinoferrosilite series to the orthorhombic enstatite-ferrosilite series is given showing that this inversion takes place at about 1145°C. for the magnesian end of the series and decreases to about 970°C. for a pyroxene very near the iron-rich end of the series.* This inversion curve was determined by heating natural orthopyroxenes containing the usual small amount of Wo so that it is more directly applicable to the pyroxenes here under consideration than would be the pure En-Fs end-members. From this curve and the observed relations mentioned above, it can be concluded that for pyrox-

---

* Inversion temperatures measured at one atmosphere pressure. At pressures obtaining under plutonic conditions some modification of the inversion temperatures might occur.

enes more magnesian than $En_{70\pm}$ the temperature of the magma was below the inversion temperature curve. Near the $MgO:FeO$ ratio of $7:3$, and for more FeO-rich pyroxenes, the temperature of the magma was on or above this curve so that a clinopyroxene, pigeonite, abruptly took the place of hypersthene. If the pigeonite were then cooled slowly, upon crossing the inversion temperature curve it would invert to hypersthene, exsolving the excess Wo as oriented augite plates (see Fig. 3).

It appears that those pigeonites in hypabyssal rocks which crystallized at a temperature very slightly above the inversion temperature have a much greater tendency to invert to hypersthene with oriented inclusions of augite, than do those more iron-rich pigeonites which probably crystallized farther above the inversion temperature. The Palisades diabase and Win Sill both are examples of this relationship. The probable reason for this is that the earlier pigeonites were held for a relatively long period at, or slightly below, the inversion temperature, thus under conditions ideal for inversion to occur. The later, more iron-rich pigeonites, passed through the inversion temperature relatively rapidly for two reasons. (1) The magma itself was decreasing in temperature rapidly during the closing stages of crystallization (note curve in Fig. 9 for change of temperature of magma with crystallization); and (2) the amount of crystallization is much less, or the magma may be completely solidified so that the heat of crystallization is diminished or zero and is no longer acting as a balance against heat lost by conduction outward from the contacts.

C. Pyroxenes as Geologic Thermometers.

From the relationship mentioned in the previous paragraph there becomes available a precise and valuable geologic thermometer. The observed pyroxenes in the Stillwater Complex, for example, must have started crystallization below 1145°C. since normal orthorhombic pyroxene is found in the early differentiates. After approximately 60 per cent of the volume of the magma had crystallized, the magma temperature crossed the inversion curve at the $MgO:FeO$ molecular ratio of $73:27$. At this point the temperature was slightly above 1100°C. The total drop in temperature from the start of crystallization to 60 per cent by volume solid appears to have been not more than 40°C. Since the other igneous bodies for which the $MgO:FeO$ ratio at which the magma temperature crossed the inversion curve also lie close to $7:3$, the temperature of the magmas of all of them must have been almost identical with that of the Stillwater magma. The inversion curve is relatively flat—a large change in $MgO:FeO$ ratio produces a small change in inversion temperature—so it appears that all of the magmas mentioned above probably were within 10°C. of each other at the start of crystallization. Inasmuch as enstatite

or bronzite with oriented plates has never been described, it seems likely that no basaltic magma before extrusion ever reached a temperature above approximately 1140°C. With considerably less certainty it can be said that normal basaltic magmas probably are intruded in all cases at a temperature above 1100°C. It may be noted here that the temperature obtained by this method for the Palisade Sill diabase magma at the time of its intrusion, 1120°C ± 10°C., lies within the limits set by Sosman and Merwin (1913), arrived at in an entirely different manner.

Wager and Deer describe a hedenbergitic clinopyroxene in the Skaergaard intrusion which formed after $98\frac{1}{2}$ per cent of the magma had crystallized. This pyroxene was interpreted on good grounds as an inverted β-wollastonite solid solution. An approximate temperature can also be
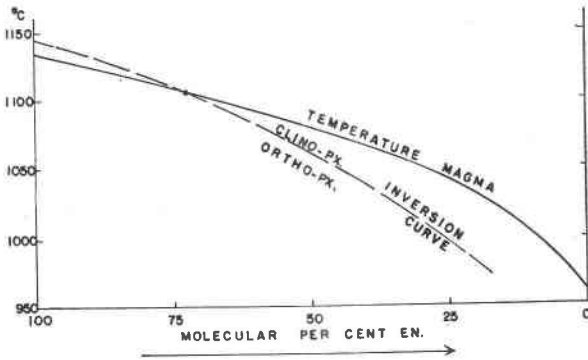

Fig. 9

placed on this inversion, 955°C. as interpolated from data given in CaO−FeO−SiO₂ by Bowen, Schairer and Posnjak. Thus a guess can be made for the final temperature of consolidation of a basaltic magma with extreme differentiation. This would place a maximum temperature difference between the start of crystallization and its virtual completion ($98\frac{1}{2}\%$) at 185°C. The estimated change in temperature of the magma with crystallization, as shown in Fig. 9, was based on this value.

A rough estimate of temperature may also be based on the calcium-rich clinopyroxenes. These clinopyroxenes occurring in contact metamorphic deposits, such as skarn, and in veins, lie very close to $Wo_{50}(En, Fs)_{50}$ in composition. They are known to have crystallized at relatively low temperatures compared to basaltic magmas. The calcium-rich clinopyroxene phases of basaltic magmas (excluding phenocrysts of effusives) have compositions for the magnesian varieties of $Wo_{40}(En, Fs)_{60}$ and for the more iron-rich varieties of $Wo_{30}(En, Fs)_{70}$. The clinopyroxenes of lamprophyres seem to lie near $Wo_{50}(En, Fs)_{50}$ indicating a very low temperature for such

magmas. The clinopyroxene found rarely in rocks of the ultramafic magma suite (Hess 1939) is also near $Wo_{50}(En, Fs)_{50}$ so far as the writer has been able to determine, this checking his previous conclusion (provided these clinopyroxenes are primary) that such magmas have relatively low temperatures.

D. Course of Crystallization of Pyroxenes from Mafic Magmas.

It has been previously shown that there is relatively little difference between pyroxene trends in mafic magmas crystallizing at depth, near

TABLE 2

Roof		Clinopyroxene	Orthopyroxene	Remarks
Skaergaard	2500 meters	Wo_{30} En_2 Fs_{68}	absent	Limit two pyroxene field→
	1800 meters	Wo_{27} En_{23} Fs_{50}	absent	
	1200 meters	Wo_{32} En_{32} Fs_{36}	Wo_9 En_{39} Fs_{52}[2]	Inverted
	500 meters	Wo_{42} En_{40} Fs_{18}[1]	Wo_9 En_{50} Fs_{41}[2]	
	0 meters	not given	Wo_9 En_{54} Fs_{37}[2]	
Covered		————	————	Pigeonites
Stillwater[3]	5400 meters	Wo_{41} En_{45} Fs_{14}	Wo_9 En_{64} Fs_{27}	
	4750 meters	Wo_{41} En_{47} Fs_{12}	Wo_4 En_{73} Fs_{23}	
	2550 meters	Wo_{41} En_{49} Fs_{10}	Wo_4 $En_{75\frac{1}{2}}$ $Fs_{20\frac{1}{2}}$	
	400 meters	Wo_{37} En_{56} Fs_7	Wo_4 En_{82} Fs_{14}	
Floor				

[1] As recalculated by the present writer allowing for Wo content in hypersthene impurity.

[2] Based on petrographical description and optical properties as given.

[3] Stillwater specimens represent either chemical analyses or pyroxenes between two analyzed specimens, estimated by optical properties.

the surface, or at the surface. Except for the phenocrysts in effusives there is no difference chemically. It is, therefore, possible to use the data derived from a large number of new analyses of Stillwater clinopyroxenes, plus the published analyses of Wager and Deer for the Skaergaard intrusion, to give the chemical changes which take place with progressive fractional crystallization. By chance the Stillwater and Skaergaard complement each other nicely. The upper portion of the Stillwater is covered and the lower portion of the Skaergaard is hidden, but the pyroxenes at the top of the former and base of the latter are closely similar so that the two sets may be joined to give the complete trends (see Table 2).

In Fig. 10 are shown the compositions of the chemically analyzed pyroxenes of the Stillwater Complex, Bushveld Complex, and the Skaergaard intrusion, plus a number of analyses of typical pyroxenes from other igneous bodies as taken from the literature. The trend of crystallization of pyroxenes is clear and has already been discussed in the descriptive
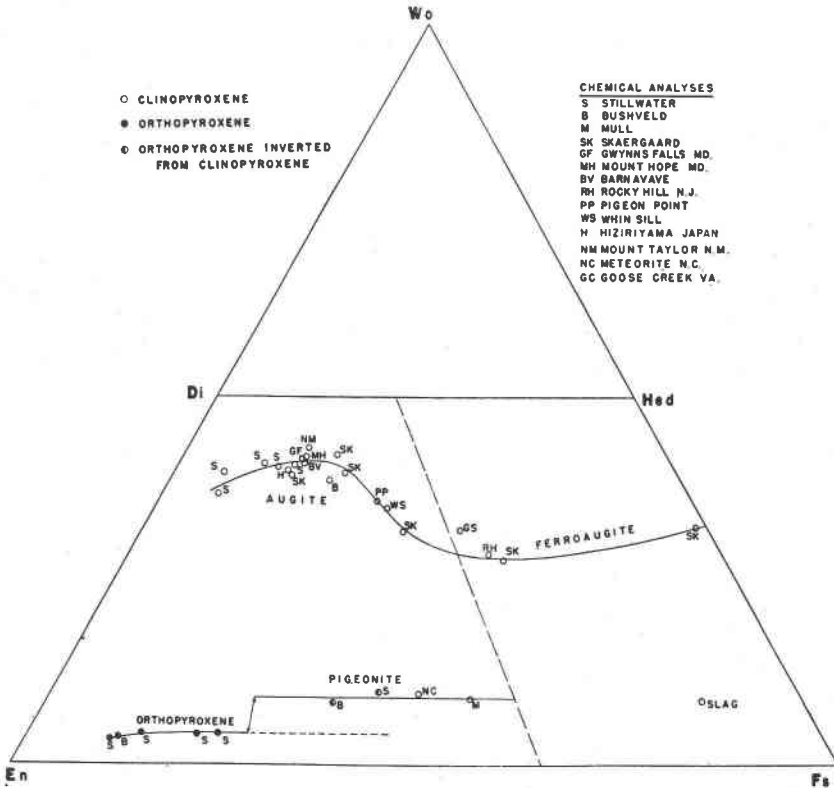

FIG. 10

portion of this paper. In Fig. 11 the relation between the composition of the augitic clinopyroxene and the orthopyroxene or pigeonite in equilibrium with it, in a given rock specimen is shown.

If a line joining the two pyroxenes of a given specimen be extended upwards to the En-Wo composition line it will intersect that line at approximately $En_{25}Wo_{75}$. Why this relationship holds the writer does not know. It is, however, a rather convenient fact to know since it may be used to predict the composition of one pyroxene from an igneous rock if the other pyroxene be known from chemical analysis or by determination from
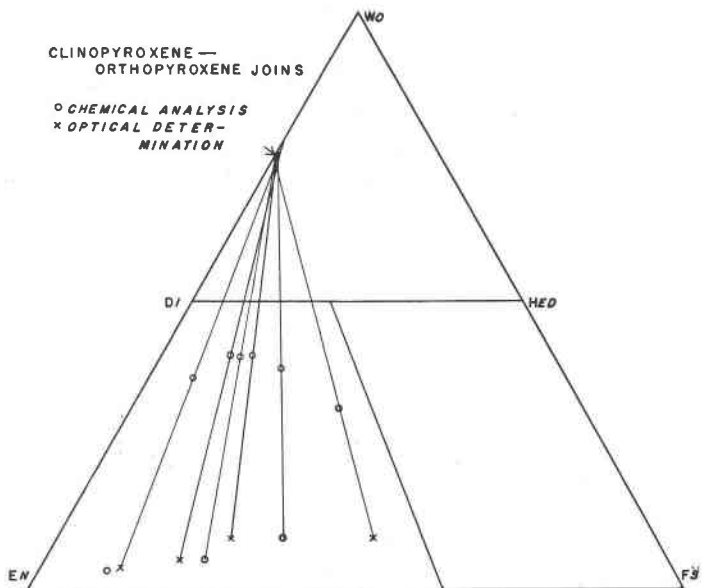
CLINOPYROXENE —
ORTHOPYROXENE JOINS

○ CHEMICAL ANALYSIS
× OPTICAL DETER-
MINATION

WO

DI   HED

EN   FS

Fig. 11

Wo
CaSiO₃

Di   A   Hed
MgCaSi₂O₆   FeCaSi₂O₆

PHENOCRYSTS
OF VOLCANICS

MINIMUM   MINIMUM

augite

TWO PYROXENE FIELD

ferroaugite

COTECTIC LINE (position doubtful)

ONE PYROXENE
FIELD

pigeonite

LIMIT 2 PX
FIELD

INVERSION

orthopyroxene

MgSiO₃   B   FeSiO₃
En   Fs
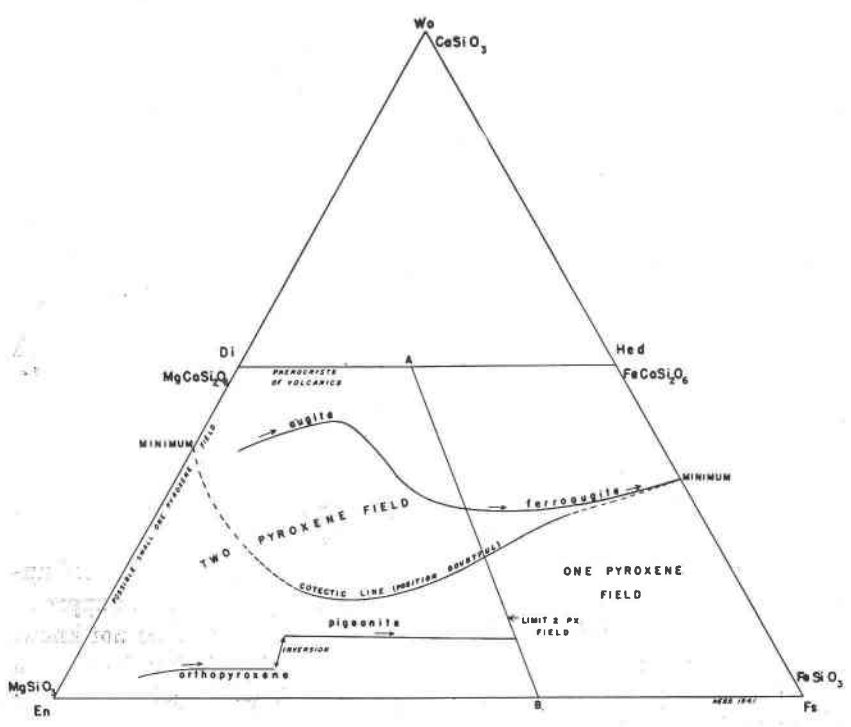
HESS 1941

Fig. 12

optical properties. It may also be used to estimate the composition of the pyroxenes in a rock for which the normative Wo:En:Fs ratio is known.

In Fig. 12 the pyroxene trends, the limit of the two pyroxene field and the two pyroxene boundary curve of Tsuboi (or cotectic) are all shown. The pyroxene portions of both the system En-Di and Fs-Hed are of the type representing a solid solution series with a minimum, according to the laboratory data of Bowen and Schairer. The two pyroxene boundary has been extended by a dashed line to join the minimum on each of the two above mentioned systems. Whether the cotectic line should be joined to the minima in this manner is not known, but it appears to be a likely approximate relationship. The position of the two pyroxene line itself is only an approximation since it is based on uncertain data. In order to locate it one must know the Wo:En:Fs ratio of a number of magmas and one must also know whether a lime-rich clinopyroxene or a lime-poor orthopyroxene or pigeonite crystallized first from that magma. Uncertainty regarding the position of this curve is related to the highly complex relations in natural magmas. The normative Wo:En:Fs ratio of fresh, fine grained, or glassy, nonporphyritic rocks might be used to locate the curve. The fact that TiO_2 and Fe_2O_3 are present in the pyroxenes themselves, however, and not all in magnetite and ilmenite, is a source of error in the location of the curve. It seems to be more satisfactory to calculate the Wo:En:Fs ratio without deducting FeO for ilmenite and magnetite where the TiO_2 and Fe_2O_3 are small in amount, and deducting only part of the FeO where they are present in greater amounts. Similarly, Al_2O_3 in the pyroxene appears as anorthite in the norm and also is a source of error. Furthermore, the presence of calcium in the magma which eventually goes into anorthite and the presence of magnesium and iron which eventually go into olivine might well have some effect on the composition of the pyroxene crystallizing even though they, later on, combined in minerals other than pyroxenes. In spite of all these difficulties it is possible to construct an approximate curve.

Following the reasoning of Tsuboi, after early crystallization of one pyroxene the second should appear and fractional crystallization should produce a successive series of liquids which would lie along the curve. If the Wo:En:Fs ratios for the more iron-rich plateau basalts be plotted, they do show a concentration along the line as given in Fig. 12.

Following the two pyroxene boundary curve to its extremity on the Ca-Fe side of the diagram, it has been joined to the minimum of Bowen's, Schairer's and Posnjak's hedenbergite-ferrosilite diagram. There is good justification for this since the final clinopyroxene of the Skaergaard intrusion has almost exactly the composition of the minimum point. The extension of the curve to the similar minimum of the diopside-enstatite

diagram was placed on the figure by analogy and has no significance so far as basaltic magmas are concerned, since these never have an MgO:FeO ratio greater than 7:3.

It has very generally been supposed that a complete series of solid solutions exists (at least at the high temperatures of laboratory investigation of dry melts) between the four components of the pyroxene series, En-Fs-Di-Hed. Justification for this view is found in the fact that the three investigated pairs, En-Di, En-Fs, and Fs-Hed bounding three sides of the field all show such a relationship. The central portion of the field has not been investigated in the laboratory, but it has been thought that natural occurrences, namely the groundmass pyroxenes of basalts and andesites, supported such an assumption. Strong evidence has been given in this paper to show that this assumption is incorrect for the natural magmas and that two pyroxene phases are normally present, at least between MgO:FeO ratios of approximately 75:25 and 35:65 (see Fig. 10). It seems likely the two pyroxene field will extend at least to a line very close to En-Di before changing over to a single series of solid solutions with a minimum if such a change takes place at all at magmatic temperatures. The trend of igneous clinopyroxenes upon approaching En-Di suggests that such a change might take place in natural magmas if magmas sufficiently iron-poor and calcium-rich could be found. Relations, however, are complicated by the presence of orthorhombic rather than monoclinic $MgSiO_3$ in rocks. On the iron-rich side of the two pyroxene field, the change represented in natural occurrences in rocks (namely the abrupt disappearance of the lime-poor pyroxene phase, pigeonite and the continued crystallization of the augitic phase along a trend which terminates almost exactly at Bowen's and Schairer's minimum in the Fs-Hed join) clearly indicates the chemical change from a field with two pyroxene phases to a field of solid solutions with a minimum. This will be further considered in a series of diagrams.

Perhaps the simplest means by which the proposed relations within the En-Fs-Di-Hed field can be discussed is by construction of a series of hypothetical equilibrium diagrams joining the En-Fs series with the Di-Hed series. The most fundamental section is one between $En_{50}Fs_{50}$ and $Wo_{50}En_{25}Fs_{25}$. This is given in Fig. 13. It must be clearly understood that this is not a true binary but a purely schematic type of diagram since the third dimension is not shown. Actually all liquidus points are far more iron-rich than solidus points, but here they are for convenience all shown in one plane. Nevertheless, the diagram illustrates qualitatively the relations in the portion of the field under consideration.

If the composition lies to the left of M, pigeonite will crystallize first, and continue to do so until point M is reached where it has the composi-

tion L and where it will be joined in crystallization by augite of composition N. After all of the liquid is used up there will remain a mixture of two solid phases, pigeonite and augite. With further decrease in temperature pigeonite becomes unstable and will invert to hypersthene T, if cooling is slow enough to permit this to occur. The change in composition from S to T in an inversion interval will result in the exsolution from S of an augite of composition R. This exsolved augite, as has been described previously, forms oriented plates in the hypersthene.

If the original composition lies to the right of M, augite will crystallize first and after the composition of the liquid reaches M, pigeonite will
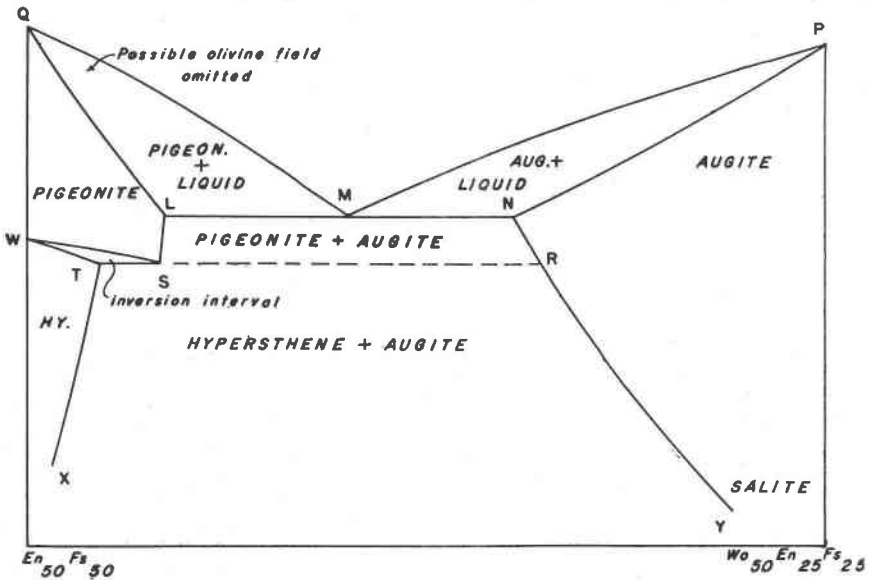

FIG. 13

start to crystallize. From this point on the sequence of events is the same as described in the previous paragraph. With continued slow cooling hypersthene changes in composition toward X, exsolving a Di-Hed pyroxene approaching Y in composition as fine lamellae parallel to (100), and augite similarly changes in composition toward Y, exsolving hypersthene which in turn forms fine lamallæ in the augite parallel to (100) or (001). As a rule this late exsolution does not go to completion, at least in the augite, because pure Di-Hed pyroxenes (+lamellæ) do not result, but rather a phase midway between N and Y. Apparently exsolution is too slow or conversely the rock cools too quickly to permit the process to go to completion, and the dissolved material will be held in solution (metastably?) indefinitely once the rock has become cold.

We may now consider how the above relations are modified in more magnesian and in more iron-rich crosssections between En-Fs and Di-Hed. If we proceed from $En_{50}Fs_{50}$-$Wo_{50}En_{25}Fs_{25}$ toward En_{100}-$Wo_{50}En_{50}$ the main change in the diagram for natural occurrences would be as follows: The inversion curve WST would move upwards relative to QM and would finally cross QM at a MgO:FeO molecular ratio near 7:3. This relationship between the inversion temperature and magma temperature is more clearly shown in Fig. 9. After WST crosses QM, hypersthene will crystallize with augite and no pigeonite will be formed since
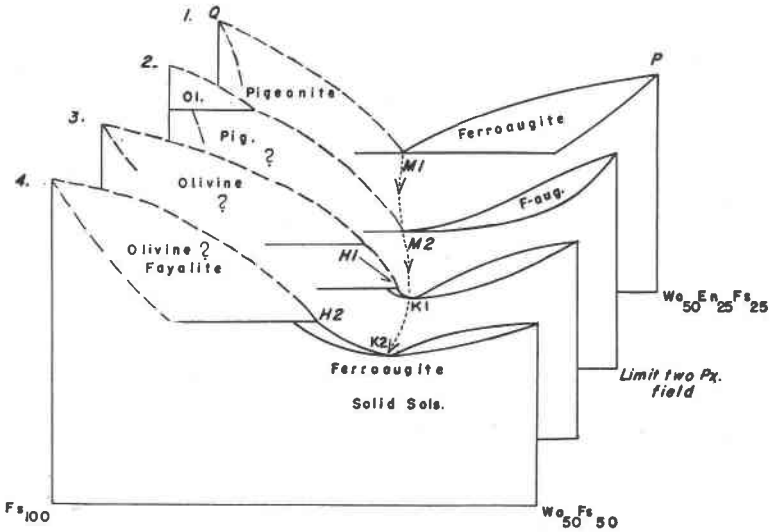

FIG. 14

crystallization is proceeding at a temperature below the stability field for pigeonite *at the MgO:FeO ratio obtaining.*

Proceeding in the other direction from $En_{50}Fs_{50}$-$Wo_{50}En_{25}$ Fs_{25} toward the more iron-rich portion of the field the following changes are thought to occur. Upon crossing the limit of the two-pyroxene field, AB Fig. 13, the augite or ferroaugite side of the diagram changes. The nature of the change is shown in Fig. 14.

Crosssection No. (1) in this figure is the same as the previous figure, and No. 4 is in part Bowen's and Schairer's diagram for Fs-Hed. Section No. 2 presents the relations at the boundary of the two-pyroxene field and No. 3 the relations just beyond the two-pyroxene field.

From section No. 1 in Fig. 14 to No. 2 the main change postulated is a narrowing of the area between the solidus and liquidus of ferroaugite. The

significant change occurs between No. 2 and No. 3 where the ferroaugite liquidus and solidus bend slightly downwards at the left hand side of the ferroaugite field developing into a solid solution series with a minimum. Crystallization in No. 1 and No. 2 had been proceeding along the cotectic line M_1–M_2 with the separation of pigeonite and ferroaugite together. At the boundary of the two-pyroxene field a change takes place the nature of which can be seen in No. 3. As a result of this change pigeonite at H in the diagram reacts with the liquid to form a ferroaugite solid solution.* After all of the pigeonite is used up, ferroaugite will continue to crystallize directly from the magma and its composition will gradually move to the minimum line K_1–K_2. It will continue to change in composition along the line K_1–K_2 as fractional crystallization proceeds until K_2 is reached, or the entire liquid becomes solid. Wager's and Deer's final clinopyroxene is practically at the point K_2. It may also be noted that an olivine field presumably appears on the left hand side of the diagram which increases in size until at the Fs-Hed join the pigeonite field has been completely removed.

It is possible as previously mentioned that a similar type of change occurs at the other side of the two-pyroxene field where the change takes place with increasing temperature to a one-pyroxene, diopside-clinoenstatite solid solution series with a minimum.

E. Summary of Main Features in Pyroxene Relations of Mafic Magmas

1. The pyroxenes of plutonic, hypabyssal and effusive mafic igneous rocks are chemically the same except for the phenocrysts of certain effusives which have been changed from augite towards diopside.

2. In a considerable portion of the field En-Fs-Di-Hed the En-Fs clinopyroxenes show limited solid solution in the Di-Hed and *vice-versa* so that both pigeonite and augite may crystallize together and commonly do.

3. Orthopyroxene bears a mutually interchangeable relationship to pigeonite. The more magnesian crystals are orthorhombic since the inversion temperature (clino- to ortho-) is above magmatic temperatures. The more ferriferous crystallize as pigeonite since the inversion temperature is below magmatic temperatures for such compositions.

4. With slow cooling pigeonite inverts to hypersthene containing oriented plates of clinopyroxene exsolved from it.

5. The most ferriferous clinopyroxenes (beyond the two pyroxene field) probably form a continuous solid solution series with a minimum, thus ferroaugite is never accompanied by pigeonite under equilibrium conditions.

* Early pigeonite phenocrysts resorbed (corroded outlines), Mull and Hakone.

6. The trend of crystallization of both the pyroxene phases is essentially from magnesian to iron-rich.

REFERENCES

1882. DOELTER, C., Vulkane der Capverden und ihre Produkte. Graz. (see Wahl, 1907).

1884. TEALL, J. J. H., Petrological notes on some North-of-England dikes: *Quar. Jour. Geol. Soc. London*, **40**, 209–247.

1887. COHEN, E., Geognostisch-petrographische Skizzen aus Süd-Africa: *Neues Jahrb., Beil. B.* **5**, 194.

1892. HOVEY, E. O., Ueber Gangdiabase der Gegend von Rio de Janeiro, etc.: *Min. Petr. Mitt. Tschermak*, **13**, 211–221.

1898. PIRSSON, L. V., Diabase, West Rock, New Haven, Conn.: *Bull. U. S. Geol. Survey*, **150**, 264–273.

1899. PHILLIPS, A. H., Mineralogical structure and chemical composition of the trap of Rocky Hill, N. J.: *Am. Jour. Sci.*, **13**, 267–285.

1900. WINCHELL, A. N., Gabbroid rocks of Minnesota, etc.: *Am. Geol.* **26**, 203.

1907. WAHL, W., Die Enstatitaugite: *Min. Petr. Mitt. Tschermak*, **26**, 1–131.

1907. BACKLUND, H., Über einige Diabase aus arktischen Gebiet: *Min. Petr. Mitt. Tschermak*, **26**, 357–390.

1913. SOSMAN, R. B., AND MERWIN, H. E., Intrusion temperature Palisades diabase: *Jour. Wash. Acad. Sci.*, **3**, 389–395.

1914. HALLIMOND, A. F., Optically uniaxial augite from Mull: *Mineral. Mag.*, **17**, 97–99.

1916. BENSON, W. N., British Antarctic Expedition 1907–9: *Geol.*, **II**, 157–160.

1918. HOLMES, A., The basaltic rocks of the Arctic Regions: *Mineral. Mag.*, **18**, 180–223.

1925. ASKLUND, B., Petrological studies in the neighbourhood of Stavsjo at Kolmården: *Årsbok Sveriges Geol. Undersök*, **17**, no. 6, 1–122.

1926. GILLSON, J. L., Pigeonite from the Triassic traps of the Connecticut Valley: *Am. Mineral.*, **11**, 317–319.

1929. FENNER, C. N., The crystallization of basalts: *Am. Jour. Sci.*, ser. 5, **18**, 225–253.

1929. HOLMES, A., AND HARWOOD, H. F., The tholeiite dikes of the north of England: *Mineral. Mag.*, **22**, 1–52.

1930. DALY, R. A., AND BARTH, T. F. W., Dolerites associated with the Karroo System, South Africa: *Geol. Mag.*, **67**, 97–110.

1931. BARTH, T. F. W., Crystallization of pyroxene from basalt: *Am. Mineral.*, **16**, 195–208.

1931*A*. BARTH, T. F. W., Hiva Oa. Marquesas-Inseln, etc.: *Neues Jahrb. Min., Beil. B.* **64**, Abt. A, 217–224.

1931*B*. BARTH, T. F. W., Mineralogical petrography of Pacific lavas: *Am. Jour. Sci.*, **21**, 377–405.

1932. TSUBOI, S., On the course of crystallization of pyroxenes from rock magmas: *Jap. Jour. Geol. and Geogr.*, **10**, 67–82.

1932. KROKSTRÖM, T., The Breven dolerite dyke: *Bull. Geol. Instit. Upsala*, **23**, 243–330.

1933. KROKSTRÖM, T., Ophitic texture and order of crystallization in basaltic magmas: *Bull. Geol. Inst. Upsala*, **24**, 197–216.

1933. BOWEN, N. L., Crystals of iron-rich pyroxene from a slag: *Jour. Wash. Acad. Sci.*, **23**, 83–87.

1933. KENNEDY, W. Q., Trends of differentiation in basaltic magmas: *Am. Jour. Sci.*, **25**, 239–256.

1933. BOWEN, N. L., SCHAIRER, J. F., AND POSNJAK, E., The system $CaO-FeO-SiO_2$: *Am. Jour. Sci.*, **26**, 193–284.

1933. TYRRELL, G. W., AND SANDFORD, K. S., Geology and petrology of the dolerites of Spitzbergen: *Proc. Roy. Soc. Edinburgh*, **53**, Pt. 3, 284–321.

1934. KUNO, H., AND SAWATARI, M., On the augites from Wadaki, Idu and from Yoneyama, Etigo, Japan: *Jap. Jour. Geol. and Geogr.*, **11**, 327–343.

1935. BOWEN, N. L., AND SCHAIRER, J. F., The system $MgO-FeO-SiO_2$: *Am. Jour. Sci.*, **29**, 153–217.

1935. LOMBAARD, B. V., On the differentiation and relationships of the rock of the Bushveld Complex: *Trans. Geol. Soc. S. Africa*, **37**, 5–52.

1935. WALKER, F., The late Paleozoic quartz-dolerites and tholeiites of Scotland: *Mineral. Mag.*, **24**, 131–159.

1935. KUNO, H., Preliminary note on the occurrence of pigeonite as phenocrysts in some pyroxene-andesite from Hakone volcano: *Jour. Geol. Soc. Jap.* **62**, 39–44.

1935. BOWEN, N. L., Ferrosilite as a natural mineral: *Am. Jour. Sci.*, **30**, 481–494.

1936. KUNO, H., On the crystallization of pyroxenes from rock-magmas with special reference to the formation of pigeonite: *Jap. Jour. Geol. and Geogr.*, **13**, 141–150.

1936*A*. KUNO, H., Petrological notes on pyroxene andesites, Hakone volcano, etc.: *Jap. Jour. Geol. and Geogr.*, **13**, 107–140.

1936. KROKSTRÖM, T., The Hällefors dolerite dike and some problems of basaltic rocks: *Bull. Geol. Instit. Upsala*, **26**, 115–263.

1936. HENDERSON, E. P., AND DAVIS, H. T., Moore County, North Carolina, meteorite—a new eucrite: *Am. Mineral.*, **21**, 215–229.

1936. BARTH, T. F. W., Crystallization process of basalt: *Am. Jour. Sci.*, **31**, 321–351.

1937. KUNO, H., Fractional crystallization of basaltic magmas: *Jap. Jour. Geol.*, **14**, 189–208.

1937. NOCKOLDS, S. R., On the fields of association of certain common rock-forming minerals: *Min. Petr. Mitt. Tschermak*, **49**, 101–116.

1938. HESS, H. H., AND PHILLIPS, A. H., Orthopyroxenes of the Bushveld Type: *Am. Mineral.*, **23**, 450–456.

1938. NOCKOLDS, S. R., Petrology of Barnavave, etc.: *Geol. Mag.*, **75**, 469–479.

1938. KUNO, H., Hypersthene from Odawara-mati, Japan: *Proc. Imp. Acad. Tokyo*, **14**, 218.

1939. HESS, H. H., Primary peridotite magma: *Am. Jour. Sci.*, **35**, 321–344.

1939. BARTH, T. F. W., AND HOLMSEN, PER, Rocks from the Antarctandes and southern Antilles: *Norske Videns. Akad. Oslo*.

1940. HESS, H. H., AND PHILLIPS, A. H., Optical properties and chemical composition of magnesian orthopyroxenes: *Am. Mineral.*, **25**, 271–285.

1940. BENSON, W. N., AND TURNER, F. J., Mineralogical notes from University Otago: *Roy. Soc. New. Zeal. Trans. & Proc.*, **69**, no. 2, 56–72.

1940. WAGER, L. R., AND DEER, W. A., Petrology of the Skaergaard intrusion: *Medd. om. Grønland*, **105**, no. 4, 335 pp.

1940. BOGUE, R., AND HODGE, E. T., Cascade andesites of Oregon: *Am. Mineral.*, **25**, 627–665.

1940. KUNO, H., Pigeonite in the groundmass of some andesite from Hakone: *Jour. Geol. Soc. Japan*, **67**, 347–351.

1940. BUGGE, J., Geological and petrological investigations in the Arendal district: *Norsk. Geol. Tidesk.*, **20**, 71–112.

1940. WALKER, F., Differentiation of the Palisades diabase: *Bull. Geol. Soc. Am.*, **51**, 1059–1106.

1940. WALKER, F., AND POLDERVAART, A., Petrology of the dolerite sill of Downes Mountain, Calvinia: *Trans. Geol. Soc. S. Africa*, **43**, 159–173.