# SOME HORNBLENDES FROM SOUTHEASTERN PENN-SYLVANIA AND DELAWARE[1]

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## ABSTRACT

A group of eight hornblendes from the Piedmont region of Pennsylvania and Delaware were studied with special reference to their genetic relationships. Chemical analyses and optical data are presented. The relationship of optical properties and composition are discussed generally. Substitution of heavy metals for magnesium has the greatest influence on optical properties. Both refractive index and optic angle $(+2V)$ increase with increasing heavy metal substitution. Substitution of aluminum for silicon has a similar effect on refractive index, but decreases the optic angle.

Potash and soda content of the hornblendes is correlated with degree of granitization of the host rock. Both total potash and the K/Na ratio in the vacant positions of the lattice increase with greater alteration.

## INTRODUCTION

The piedmont province in Pennsylvania and Delaware has been studied for many years from a structural and petrologic standpoint. Excellent detailed studies of the petrography and structure of the metamorphic rocks in the area are available, but the mineralogy of the more complex constituents of these rocks has been neglected. A more thorough knowledge of the chemical characteristics of such common, but complex, silicates as the pyroxenes, amphiboles, micas, and garnets which occur in these rocks would be of great value in the interpretation of petologic phenomena. This paper, together with the recent work of Clavan, Mcnabb and Watson (1954) on the ortho-pyroxenes of this region, is meant as the beginning of such a study of these minerals.

The regional geology has been described in several folios covering the area (Bascom et al. 1909, 1920, 1932). The major rock types in the area are metagabbros, migmatites, and granite gneisses of pre-Cambrian age, metamorphosed sediments (schists, phyllites and limestones) of pre-Cambrian or early Paleozoic age, and Triassic sediments of the Newark series. The age and structure of many of these rocks is still a matter of controversy and these questions are not discussed here.

This paper deals with the mineralogy and petrologic relationships of some hornblendes from the metamorphic rocks in the area.

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## Occurrence of the Hornblendes Studied

The samples taken for separation of hornblendes for analysis represent several different but characteristic rock types of the Piedmont region. Individual samples were selected in such a way as to be representative of the rock type and at the same time have the least variation. In order to obtain valid correlations between rock type, hornblende composition, and hornblende properties the samples were taken from a single outcrop chosen for the uniformity of its material. The locations of the samples are listed below, including a grid index on the 15 minute quadrangle maps for the area.

*35-2*—Chester 14373—500 feet northeast of Upper Bridge, Crum Creek Reservoir. A course-grained pegmatoid schlieren in Baltimore gneiss. In the immediate area there are numerous gabbroic xenoliths in varying stages of alteration or assimilation by felsic material.

*35-5*—West Chester 92755—0.1 mile north of crossroads at Tallyville, Delaware (U. S. Route 202). A medium fine-grained eucritic norite showing a slight gneissic banding; a portion of the variable metagabbro mass known as the Wilmington gabbro.

*35-10*—Wilmington 17328—White Clay Creek west of bridge on Delaware Route 2. A hornblende gneiss alternating with bands of granite gneiss. Small stock-like intrusions of microcline rich pegmatites cross-cut both rock types. These rocks are grouped with the Port Deposit granodiorite which is intrusive into the Wilmington gabbro.

*35-11*—Elkton 63651—300 feet west of bridge over Christiana Creek. A very coarse-grained portion of the Wilmington gabbro which becomes still coarser to the northeast, and finer-grained and more massive on Chestnut Hill and Iron Hill to the southwest.

*35-22*—Norristown 89781—Small quarry on knoll 0.5 mile southwest of Ithan Creek and Bryn Mawr Avenue. A hornblende gneiss member of the Wissahickon formation. These hornblende gneisses have been described in detail by Weiss (1949).

*35-27*—Chester 29959—Center of Springfield Granite Quarry. A 1 to 3 foot wide band of hornblende-biotite schist in the Springfield granodiorite. This rock type has been shown by Postel to be a granitized equivalent of the hornblende gneiss members of the Wissahickon schist.

*35-29*—Burlington 18779—Van Artsdalen's Quarry. A massive medium-grained gabbro in the form of "boudins," from broken and deformed dikes enclosed in coarse marble which is surrounded by a dioritic gabbro. Some of the metagabbros within the quarry are rich in scapolite. A detailed discussion of the petrology of this area is given by Weiss (1947).

*35-31*—Wilmington 22458—Cut on the Landenburg Branch of the Baltimore and Ohio Railroad, 0.5 mile northeast of Marshaltown, Delaware. A medium-grained, massive metagabbro belonging to the Wilmington gabbro mass. Locally the quartz content becomes very high, and occasional narrow veins of quarts cross cut the rock.

A volume per cent analysis made on thin sections of the samples described above is given in Table 1.

## Separation of the Hornblendes

### Crushing and Optimum Grain Size

The crushing of the relatively large quantities of material needed was readily accomplished by use of a small jaw crusher, a roller mill, and a

TABLE 1

| Sample | 35-2 | 35-5 | 35-10 | 35-11 | 35-22 | 35-27 | 35-29 | 35-31 |
|---|---|---|---|---|---|---|---|---|
| hornblende | 28 | 21 | 58 | 56 | 59 | 38 | 67 | 36 |
| augite | — | 8 | — | — | — | — | 11 | 5 |
| hypersthene | — | 10 | — | — | — | — | — | — |
| plagioclase | | | | | | | | |
| comp. | $An_{30}$ | $An_{72}$ | $An_{34}$ | $An_{66}$ | $An_{37}$ | $An_{34}$ | $An_{51}$ | $An_{57}$ |
| albite | 18 | 16 | 20 | 14 | 9 | 20 | 10 | 15 |
| anorthite | 8 | 41 | 11 | 28 | 5 | 10 | 11 | 26 |
| potash feld. | 2 | — | — | — | — | — | — | — |
| quartz | 24 | — | 5 | — | 20 | 6 | — | 8 |
| biotite | 16 | — | 3 | — | — | 20 | — | — |
| magnetite | 4 | 4 | — | 1 | 7 | — | 3 | 10 |
| clinozoisite | — | — | 3 | 1 | — | 3 | — | — |
| sphene | — | — | — | — | — | 3 | — | — |

ball mill, in that order. The crushed material was sieved, and the 100 to 150 mesh fraction was taken for separation.

In almost all cases material coarser than 100 mesh contained too many combined grains, that is, grains composed of more than one mineral. As the grain size is decreased from 150 mesh, separation operations become more difficult. The fraction between 100 and 150 mesh has the least number of combined grains, is easy to handle in separation, and can be used directly for chemical analysis and optical study.

*Separation Methods*

Prior to the separation itself it was found necessary to remove all dust or finely ground material from the sample. This was accomplished by wet screening the sample on a 200 mesh screen and drying after the removal of the excess water by acetone. Dust free grains give better separations by magnetic methods, and are easier to wash in heavy liquid separations. Removal of water prior to drying lessens the danger of oxidation of ferrous iron present in the sample.

A good separation of hornblende from most of the constituents of the rocks in question can be easily and rapidly made by use of the Franz isodynamic separator (Franz in Gaudin and Spedden, 1943). The following procedure was used:

(*a*) The feeder trough of the separator was set at an angle of 25° parallel to it and 15° at right angles to it. This trough orientation was found satisfactory for all steps.

(*b*) Highly magnetic material such as magnetite, ilmenite, and pyrrhotite was first removed by a hand magnet.

(*c*) The material was then passed through the separator at a very low intensity field (0.1 ampere). This removed such minerals as hematite, limonite, pyrite, and magnetite present as inclusions in the grains. The non-magnetic fraction was passed through once or twice more: being the fraction of greater volume it sweeps some of the magnetic material along with it and several passes are necessary for a complete separation. This procedure of repeated separations at the same field intensity was followed in all subsequent steps.

(*d*) The non-magnetic portion from (*c*) was run through at a high field intensity (1.0 ampere). This separates most of the mafic minerals from quartz and feldspar.

(*e*) Several passes were made on the magnetic fraction from (*d*) at intensities gradually increasing from that in (*c*). These steps removed minerals more magnetic than hornblende such as hypersthene and garnet.

(*f*) Several passes were then made on the non-magnetic fraction from (*e*) at intensities gradually decreasing from (*d*). These steps removed minerals less magnetic than hornblende, such as muscovite, diopside, and most augites.

This general procedure often resulted in the concentration of hornblende to 90 per cent or better. In some cases, however, large amounts of iron rich biotite and augite were present, and the hornblendes could not be separated from them by the isodynamic separator.

Further separation and purification of the samples was accomplished by heavy liquid techniques. By initial use of magnetic separation the volume of sample was reduced sufficiently for these methods to be practicable. Felsic minerals were removed by bromoform. Augite and biotite were removed by methylene iodide whose specific gravity was adjusted to points just above and below that of the hornblende by the addition of small amounts of acetone.

The sample taken for analysis was examined for purity and, where necessary, some hand picking was done. All samples analyzed contained no more than traces of foreign minerals.

### Non Uniformity of Mineral Grains

Several of the hornblendes encountered were found to have a rather large range in specific gravity. Optical examination of these samples especially in thin section showed a marked color zoning of individual grains. It was assumed that these samples were variable in composition, and they were discarded from this work.

## CHEMICAL COMPOSITION OF THE HORNBLENDES

### *Discussion of Analytical Methods*

The analytical procedure used was essentially that as outlined by Washington (1930) for the analysis of silicate rocks, with slight modifications for the specific problems at hand. Although the analyses are reported to the second decimal, this last place is not regarded as really significant. Errors inherent in the analytical methods as well as those introduced by the slight variation in composition of the mineral do not permit such precision.

In all of the analyses, material of 100–150 mesh was used except in the alkali determinations where the sample was ground to −325 mesh. Alkalies were determined by the J. Lawrence Smith method. Total iron was determined on the total $R_2O_3$ group by reduction with hydrogen sulfide and titration with permanganate. Ferric iron and aluminum were determined by difference. Water was determined by the Penfield method. Some of the specific analytical procedures are given in greater detail below:

*Ferrous Iron*—The problem of oxidation of ferrous iron during grinding was almost completely eliminated by the use of coarse-grained (100-150 mesh) samples. The decomposition was effected readily and rapidly by use of a sulfuric-hydrofluoric acid mixture in a covered platinum crucible. Titration of the resulting solution with permanganate gave reproducible results.

*Fluorine*—The fluorine determination was carried out according to the method of Willard and Winter (1933), with slight modification adapting it to the analysis of glass.* In brief the method is as follows: A mixture of 1 part sample, 1.5 parts ZnO and 10 parts $Na_2CO_3$ is fused in a platinum dish. The fusion is disintegrated and digested with hot water, and filtered into the distillation flask.† The flask is connected to the still head and 15 cc.of concentrated sulfuric acid are added dropwise. The solution is boiled until a temperature of 135° C. is reached, and the distillate is collected. The solution is maintained at this temperature until an additional 100 cc. of distillate is obtained. The distillate is made alkaline to phenolpthalein, by the addition of dilute NaOH, and is evaporated to a volume of 25 cc. The solution is cooled and 25 cc. of 95% ethyl alcohol are added. Five drops of sodium alizarin sulfonate are added and the solution acidified with dilute HCl. The fluosilicic acid now in solution is titrated with a standard thorium nitrate solution to the formation of a pink lake with the indicator reagent.

*Silica*—The presence of appreciable amounts of fluorine in silicates causes a low value for silica, due to the loss of a small amount as the tetrafluoride during the fusion. In most cases the amount of fluorine present was small enough so that the addition of a small amount of borax to the carbonate fusion was sufficient to remove almost all of the fluorine and prevent its interference (Hillebrand & Lundell, p. 537).

*Water*—Hygroscopic water was not determined. Since the samples were subjected to

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* Personal communication, H. S. Moser, Kimble Glass Co., Vineland, New Jersey.

† The apparatus, described by Willard and Winter, was made by the Scientific Glass Apparatus Co., Bloomfield, New Jersey.

repeated washings with both water and acetone prior to the analysis, it is believed that a determination of this constituent would be meaningless.

## DISCUSSION OF THE ANALYSES

The complete analyses of eight hornblendes of the southeastern Pennsylvania-Delaware area are given in Table 2. The significance of the differences is more fully discussed in the section on atomic constitution, but several marked differences and similarities in composition can be pointed out here.

TABLE 2

| Sample | 35-2 | 35-5 | 35-10 | 35-11 | 35-22 | 35-27 | 35-29 | 35-31 |
|--------|------|------|-------|-------|-------|-------|-------|-------|
| $SiO_2$ | 42.90 | 44.94 | 45.09 | 48.71 | 42.65 | 45.28 | 43.33 | 44.73 |
| $Al_2O_3$ | 11.92 | 11.24 | 10.43 | 9.48 | 15.89 | 11.00 | 15.28 | 11.54 |
| $TiO_2$ | 1.44 | 1.79 | 0.84 | 0.32 | 0.65 | 1.01 | 1.23 | 1.32 |
| $Fe_2O_3$ | 5.04 | 2.87 | 3.90 | 2.33 | 5.33 | 4.42 | 1.11 | 2.87 |
| FeO | 12.58 | 12.61 | 10.14 | 9.12 | 14.69 | 10.50 | 8.89 | 11.07 |
| MgO | 10.30 | 11.98 | 12.52 | 14.43 | 6.64 | 12.02 | 13.77 | 11.89 |
| MnO | 0.30 | 0.22 | 0.24 | 0.23 | 0.43 | 0.28 | 0.13 | 0.40 |
| CaO | 11.49 | 11.61 | 12.29 | 11.93 | 10.13 | 12.48 | 12.15 | 11.83 |
| $Na_2O$ | 2.40 | 1.86 | 1.60 | 1.16 | 2.08 | 1.59 | 2.41 | 1.45 |
| $K_2O$ | 1.19 | 0.47 | 0.78 | 0.15 | 0.28 | 0.97 | 0.87 | 0.60 |
| $H_2O$ | 1.32 | 1.26 | 1.76 | 1.83 | 1.64 | 1.02 | 0.85 | 1.79 |
| F | 0.20 | 0.24 | 0.28 | 0.23 | 0.27 | 0.31 | 0.73 | 0.16 |
| Cl | tr. | — | — | — | — | — | 0.06 | — |
| Total | 101.08 | 101.09 | 99.87 | 99.92 | 100.68 | 100.82 | 100.81 | 99.65 |
| O for F | 0.08 | 0.10 | 0.12 | 0.10 | 0.11 | 0.13 | 0.32 | 0.07 |
| Corr. total | 101.00 | 100.99 | 99.75 | 99.82 | 100.57 | 100.69 | 100.49 | 99.58 |

Silica content is generally low, except in 35-11 where it is higher and associated with a lower alumina. Alumina is unusually high in 35-22 and 35-29. Sample 35-22 is unique in its very high iron content, low calcium and high sodium content.

Titania is interesting in that it varies by a factor of as much as five. Although the total amount of this metal is not great it is believed that it has a marked influence on the color of the hornblende.

Variations in the alkalies are also of special interest. High potash content generally corresponds to a relatively high soda content. The converse is not necessarily true. High soda may be more closely correlated with high alumina. Samples 35-2 and 35-27, showing the highest potash content, are from areas generally regarded as having been granitized.

Fluorine content is generally low and constant. Sample 35-29, associ-

ated with the scapolite metagabbro, has a higher fluorine and an appreciable chlorine content.

## ATOMIC CONSTITUTION OF THE HORNBLENDES

The most useful and significant method of representing mineralogical compositions is in terms of mole per cent of each element present. This method is useful because it gives the true proportion between the various constituents. In the case of many silicate minerals the crystal structure has been determined, making it possible to determine the actual number of atoms of each element in a unit cell of the structure. Where several isomorphous substitutions are taking place simultaneously it is difficult to follow them when a mole per cent representation is being used, but an atoms per cell representation makes all the steps immediately apparent. The structure of tremolite has been determined by Warren (1929), and by the applications of Pauling's rules of isomorphous substitution he has discussed the nature of the structure of the more complex amphiboles such as hornblende. Since this structure has been almost universally accepted, it was assumed in the recalculation of the present analyses. In Table 3 the composition of the analyzed hornblendes is given in terms of

TABLE 3

| Sample | 35-2 | 35-5 | 35-10 | 35-11 | 35-22 | 35-27 | 35-29 | 35-31 |
|---|---|---|---|---|---|---|---|---|
| Si | 6.38 | 6.62 | 6.65 | 6.99 | 6.34 | 6.67 | 6.32 | 6.59 |
| $Al_s$* | 1.62 | 1.38 | 1.35 | 1.01 | 1.66 | 1.33 | 1.68 | 1.41 |
| $Al_y$* | 0.47 | 0.57 | 0.46 | 0.59 | 1.13 | 0.58 | 0.95 | 0.60 |
| Ti | 0.16 | 0.19 | 0.09 | 0.03 | 0.07 | 0.11 | 0.13 | 0.15 |
| $Fe'''$ | 0.56 | 0.32 | 0.43 | 0.25 | 0.60 | 0.49 | 0.12 | 0.32 |
| $Fe''$ | 1.56 | 1.55 | 1.25 | 1.09 | 1.82 | 1.29 | 1.09 | 1.36 |
| Mg | 2.28 | 2.63 | 2.74 | 3.09 | 1.46 | 2.62 | 3.00 | 2.61 |
| Mn | 0.04 | 0.03 | 0.03 | 0.03 | 0.05 | 0.04 | 0.02 | 0.05 |
| Ca | 1.83 | 1.83 | 1.94 | 1.84 | 1.62 | 1.97 | 1.90 | 1.87 |
| Na | 0.69 | 0.53 | 0.46 | 0.32 | 0.60 | 0.46 | 0.68 | 0.42 |
| K | 0.22 | 0.09 | 0.15 | 0.03 | 0.05 | 0.18 | 0.16 | 0.12 |
| OH | 1.30 | 1.24 | 1.73 | 1.76 | 1.63 | 1.01 | 0.83 | 1.76 |
| F | 0.10 | 0.12 | 0.13 | 0.10 | 0.13 | 0.14 | 0.33 | 0.07 |
| Cl | — | — | — | — | — | — | 0.02 | — |
| Y group | 5.07 | 5.29 | 5.00 | 5.08 | 5.13 | 5.13 | 5.29 | 5.09 |
| $Mg+Al_y/Y$ | 0.54 | 0.61 | 0.64 | 0.72 | 0.51 | 0.62 | 0.75 | 0.63 |
| Na+K in AA' | 0.74 | 0.45 | 0.55 | 0.19 | 0.27 | 0.61 | 0.74 | 0.41 |
| $Fe'''/Fe''$ | 0.36 | 0.21 | 0.34 | 0.23 | 0.33 | 0.38 | 0.11 | 0.24 |

* Sufficient aluminum was taken to make up the number of metal atoms in the chain to eight. This aluminum is designated as $Al_s$ while the remainder is assumed to replace Mg and is designated as $Al_y$.

atoms per unit cell calculated on the basis of a total of 24 atoms of oxygen, fluorine, and hydroxyl groups. The general formula of the amphiboles as given by Larsen and Berman (1931) is as follows:

$$(Ca, Na)_2(Na, K)_{0-1}Mg(Mg, Al)_4(Al, Si)_2Si_6O_{22}(O, OH, F)_2.$$
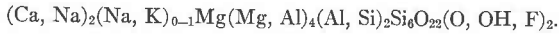
In this work the group $[Mg(Mg, Al)_4]$ will be refered to as the Y group. Within it the following additional substitutions may take place. $Fe''$ and $Mn''$ may replace the Mg, and $Fe'''$ and Ti may replace the Al. If the values given in Table 3 are compared to this general formula, they will be seen to correspond quite closely.

Since many of the isomorphous substitutions are such that elements of different valencies may replace each other, it is obvious that they cannot be completely independent variables; a deficiency caused by one replacement must be made up in a second one. The replacement of silicon by aluminum in the chains tends to activate the oxygens of the chain and permit the introduction of alkalies in the so-called vacant positions AA' of the lattice (Warren, 1930). The effect of the Si-Al replacement may also be offset by the introduction of trivalent atoms in the Y group. A crude but definite proportionality between aluminum in the chain and total alkalies may be seen in the data given. The number of hydroxyl groups plus fluorine often falls below two, the difference supposedly being oxygen. This is to be expected if the content of trivalent atoms in the Y group rises to a high value, and indeed is typical of the oxyhornblende or basaltic hornblende in which the ferric iron content is very high. The Y group total occasionally increases to about five per cent over its correct value of 5. This is apparently not uncommon in hornblende analyses (Hallimond, 1943), but no attempt at explaining it seems to have been made. The smaller deviations from the total of five might be accounted for by the normal errors of the analysis, since the errors would be cumulative. The larger deviations, however, seem too large to be explained in this way. The only solution which seems to suggest itself is that a small amount of magnesium, in spite of its appreciably smaller ionic radius, may replace calcium.

## PHYSICAL PROPERTIES OF THE HORNBLENDES

### *Specific Gravity*

Specific gravities of the hornblendes were determined by the pycnometer method. Boiled, distilled water to which a trace of detergent was added as a wetting agent was the medium used. The density of this medium at 20° C. was 0.9986 g./cc. The specific gravities, as shown in Table 4, vary from 3.115 in the actinolitic member (35-11) to 3.234 in the iron and aluminum rich member (35-22). From the substitutions

known to be possible in the amphibole molecule, it can be predicted that
the greatest effect on specific gravity would be that due to the substitu-

TABLE 4

| Sample | Sp. G. $\pm 0.002$ |
|--------|--------------------|
| 35-2 | 3.203 |
| 35-5 | 3.204 |
| 35-10 | 3.153 |
| 35-11 | 3.115 |
| 35-22 | 3.234 |
| 35-27 | 3.181 |
| 35-29 | 3.175 |
| 35-31 | 3.192 |

tion of heavy ions such as $Fe''$, $Fe'''$, and $Ti''''$ in the Y group in place
of $Mg''$. Replacement of either $Mg''$ or $Si''''$ by $Al'''$ would have little
effect insofar as changing the molecular weight of the molecule. Substitu-
tion of aluminum in the chain, however, might have a considerable
effect on the cell volume and would therefore influence the specific grav-
ity. Data on cell dimensions of amphiboles is sparse (Warren, 1930), but
an estimated change in unit cell volume of 0.5 per cent is probably
not excessive. Such a change in unit cell volume would cause a change
of about 0.01 in specific gravity. Figure 1*a* shows the relationship of
specific gravity to increasing value of the $Mg + Al_y/Y$ ratio (equivalent
to decreased heavy metals in the Y position). It will be noted that where
points deviate from the line drawn, those lying above it generally have a
large amount of aluminum in the chain. Where high aluminum is com-
bined with low heavy metals (35-29) this deviation is greatest. The horn-
blende 35-29 is unique in all of its physical properties and, as will be seen
later, should properly be called pargasite.

## OPTICAL PROPERTIES

Table 5 lists the optical properties of the eight analyzed hornblendes.
Refractive indices were determined by the immersion method, using li-
quids whose indices were spaced about 0.0025 apart. The accuracy of
index determinations is estimated as $\pm 0.001$. The optic angle and orien-
tation were determined on a four circle universal stage. Since one optic
axis generally fell outside the range of the stage, it was necessary to
determine the optic angle by measuring V rather than 2V. This reduced
the accuracy of these measurements to about $\pm 3$ degrees. The values of
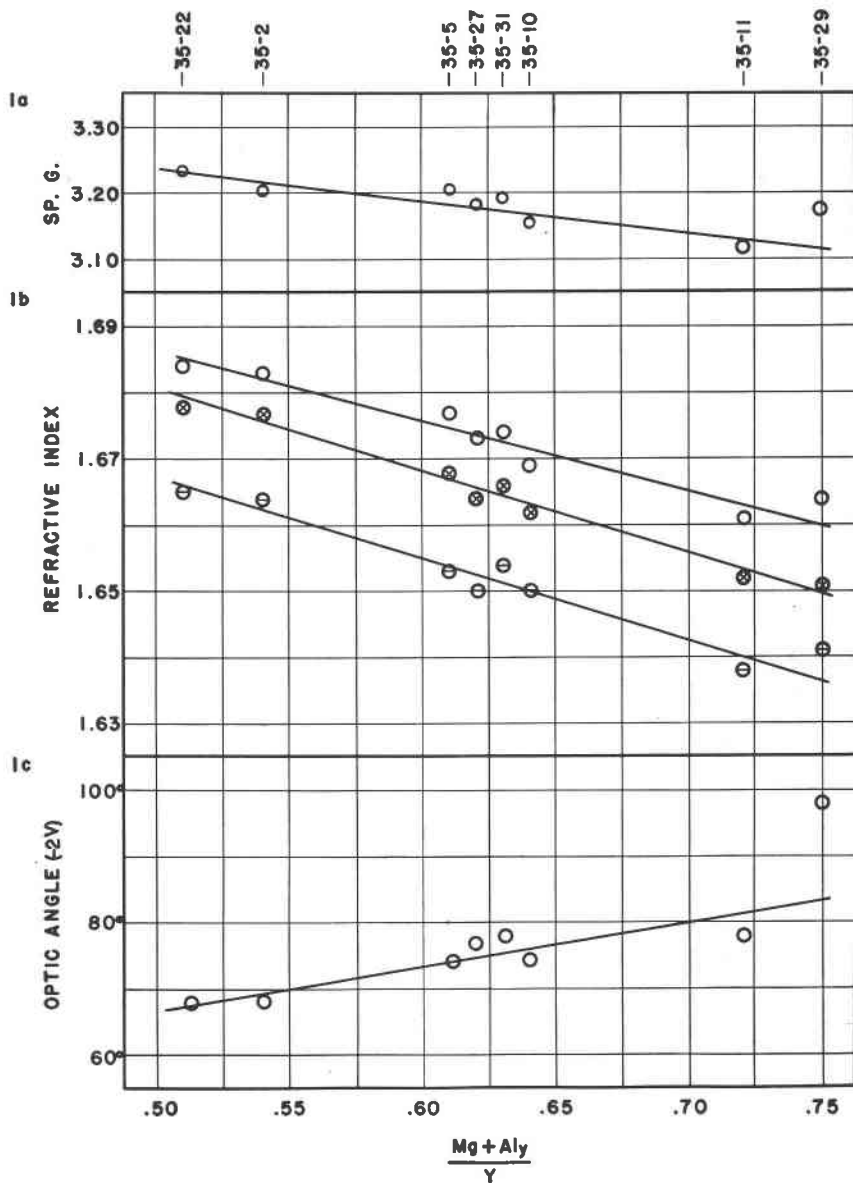optic angles calculated from the refractive indices are in good agreement

Fig. 1

with the measured values. All of the above measurements were made by sodium light. Pleochroic colors were observed on thin sections of standard thickness on the universal stage. An ordinary tungsten filament light source with a thin blue filter was used.

TABLE 5

| Sample | 35-2 | 35-5 | 35-10 | 35-11 | 35-22 | 35-27 | 35-29 | 35-31 |
|---|---|---|---|---|---|---|---|---|
| $\alpha$ | 1.664 | 1.653 | 1.650 | 1.638 | 1.665 | 1.650 | 1.641 | 1.654 |
| $\beta$ | 1.677 | 1.668 | 1.662 | 1.652 | 1.678 | 1.664 | 1.651 | 1.666 |
| $\gamma$ | 1.683 | 1.677 | 1.669 | 1.661 | 1.684 | 1.673 | 1.664 | 1.674 |
| $\gamma-\alpha$ | 0.019 | 0.024 | 0.019 | 0.023 | 0.020 | 0.023 | 0.023 | 0.020 |
| $Z\wedge c$ | 15° | 16° | 17° | 18° | 19° | 17° | 22° | 19° |
| $-2V$ | | | | | | | | |
| meas. | 65° | 72° | 72° | 78° | 67° | 75° | 98° | 78° |
| calc. | 68° | 74° | 74° | 78° | 68° | 77° | 98° | 78° |
| Pleochroism* | | | | | | | | |
| X | brn-y | p y | y | p y | y | p y | y | y-grn |
| Y | y-grn | y-grn | grn | lt grn | grn | lt grn | y-brn | lt grn |
| Z | d bl-grn | brn-grn | bl-grn | lt bl-grn | bl | bl-grn | lt brn | d grn |

* Abbreviations used in color descriptions: y—yellow; bl—blue; grn—green; brn—brown; p—pale; d—deep; lt—light.

The complexity of hornblende composition presents a very definite problem in approximating composition from optical data. In spite of the fact that many of the isomorphous substitutions are interdependent, there still may be as many as five or six factors influencing a particular optical property. With any convenient method it can be hoped only to determine the ratios of a few of the constituents; those which have the strongest effect on the optical properties. Winchell (1945) has tabulated the properties of approximately one hundred calcic amphiboles on a partial triangular prism. There are eight end-member molecules in this system as follows:

$Ca_2Mg_5Si_8O_{22}(OH)_2$            $Ca_2Fe''_5Si_8O_{22}(OH)_2$

$Ca_2Mg_3Al_4Si_6O_{22}(OH)_2$        $Ca_2Fe''_3Fe'''_2Al_2Si_6O_{22}(OH)_2$

$NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2$     $NaCa_2Fe''_4Fe'''Al_2Si_6O_{22}(OH)_2$

$NaCa_2Mg_5AlSi_7O_{22}(OH)_2$       $NaCa_2Fe_5AlSi_7O_{22}(OH)_2$

In addition to this diagram, a similar one for the oxyhornblendes is given. In any actual case a combination of the two would be necessary since most common hornblende contains some of the oxyhornblende molecule. In the actual plotting of data in this prismatic diagram Winchell combines ferric and ferrous iron and assumes that the calcium content is constant. Combining the irons fails to distinguish their effect,

and unless it is assumed that the $Fe''/Mg$ ratio is the same as the $Fe'''/Al_y$ ratio in any one hornblende, the significance of the ferric iron end members is lost. An examination of the data given in Table 3 shows that the assumption is not valid. It is, however, necessary to combine these constituents if we wish to give even an approximate graphical representation of their effect on optical properties. As his four variables Winchell uses the following: (*a*) the number of atoms of silicon minus *6;* (*b*) the number of aluminum atoms in the chain; (*c*) the number of atoms of alkali metals in the vacant position; and (*d*) the ratio of light metals in the Y group to the total Y group $(Mg+Al_y/Y)$. The data obtained on the present hornblendes were plotted on Winchell's diagram. The index $\gamma$ was found to be generally lower than would have been predicted from the diagram; other properties were in good agreement.

Figure 1*b* and 1*c* show the variation of optical properties with increasing $Mg+Al_y/Y$ ratio, that is with decreasing heavy-metal substitution in the Y group. Refractive indices decrease with an increase in this ratio while the optic angle $-2V$ increases. Birefringence measurements are subject to too great an error to be correlated accurately, but this value is generally found to increase with this ratio. It will be noted that the values for sample 35–29 show the greatest deviation from the line drawn, as was the case with the specific gravity plot. Increased substitution of aluminum for silicon is probably responsible for this effect. This substitution appears to increase refractive index as well as the optic angle $-2V$.

The transition of the color of hornblendes from brown to green has been discussed in detail by Deer (1938). He has shown that the brown color of ordinary hornblendes is not due to the ferric iron content but rather to titanium. In the oxyhornblendes where the ratio $Fe'''/Fe''$ rises to values of well over unity the influence of the ferric ion will have a marked effect. In the ordinary hornblendes the value of this ratio is usually below unity and in the present case it is appreciably less. At any given $Fe''$ content, according to Deer, an increase of Ti should give a browner color in the Z direction. A rough correlation between increasing value of the $Fe''/Fe''+Ti$ ratio and a change in color in the Z direction from brown to green is given in Table 6.

## MAGNETIC PROPERTIES

During separation by means of the Frantz isodynamic separator, it was noted not all of the hornblendes were removed at the same field intensity. Under the conditions of separation the range in field intensities was very slight, amounting to current changes of less than 0.1 ampere. By changing the angle perpendicular to the feeder trough to 30° rather than 15° this range was spread to about 0.3 ampere. The effect of increasing this

TABLE 6

| Sample | Fe''/Fe''+Ti | Color on Z |
|--------|--------------|------------|
| 35-29 | 0.83 | light brown |
| 35-5 | 0.89 | brownish green |
| 35-31 | 0.90 | deep green |
| 35-27 | 0.92 | blue green |
| 35-2 | 0.92 | deep blue-green |
| 35-10 | 0.93 | blue-green |
| 35-22 | 0.96 | blue |
| 35-11 | 0.97 | light blue-green |

angle is to make the magnetic field work against gravity to a greater extent. A series of careful measurements were made of the current necessary to deflect each of the hornblendes. The results were plotted against the $Mg+Al_y/Y$ ratio of the hornblende. The current required is inversely proportional to the heavy metal content of the mineral. Such a technique may be useful in approximating the iron or iron plus titanium content of silicate minerals, providing that the conditions of the experiment are kept constant. The data presented in Fig. 2 were obtained under the following conditions: The orientation angles of the trough were 25° parallel, and
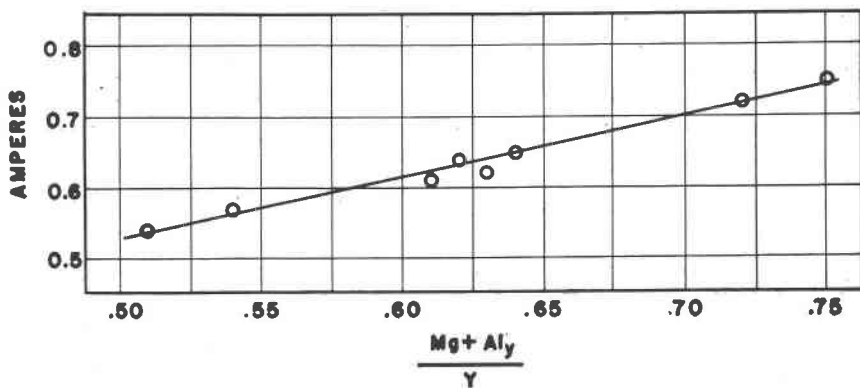


FIG. 2

30° at right angles; the rate of feed was approximately 1 gram per minute; the current was read at that point where the hornblende was divided equally between the magnetic and non-magnetic fraction.

## GENETIC RELATIONSHIPS OF THE HORNBLENDES

### Origin of Hornblendes in General

Hornblendes may originate through either magmatic or metamorphic processes. It is well to restrict magmatic processes to primary crystallization, leaving the alteration of previously formed minerals by residual solutions of magmatic processes to the metamorphic group. Of the hornblendes described here none were formed by purely magmatic processes. The metamorphic processes may be subdivided as follows: (a) purely dynamic processes (assuming the necessary water to be already available in the rock); (b) contact metamorphic processes, either with or without the addition of new material; (c) hydrothermal processes, either with or without the introduction of new material other than water. An examination of these processes shows that there are three factors controlling the composition of the hornblende formed in or from any particular rock type. First, the original composition of the rock; second, the nature of the new materials introduced; and third, the process by which these new materials are added. The greatest proportion of the hornblendes in the Piedmont area were probably formed by hydrothermal or contact processes during large scale regional metamorphism.

A generalized relationship between parent rock and the composition of the hornblende it contains is given by Hallimond (1943). The composition of nearly two hundred hornblendes are plotted on a partial triangular diagram using the number of silicon atoms per cell as one coordinate, the number of aluminum atoms in the chain as the second, and the number of alkali ions in the vacant position as the third. The points for hornblendes occurring in similar tock types were found to lie in certain general fields of the diagram. Hallimond's diorite field includes such rocks as syenites, gabbros and hornblende gneisses. Two fields appear for limestone, one to represent ordinary hornblende and one to represent pargasite. The pargasitic field probably represents those limestones to which material has been added during metamorphism. All of the hornblendes with the exception of 35–29 are closely related to gabbroic rocks or hornblende gneisses, and fall within the diorite or amphibolite fields of Hallimond. The composition of sample 35–29, which occurs in a metagabbro inclusion within limestone, falls in the pargasite field.

Deer (1938) has discussed a group of nine hornblendes from the Glen Tilt complex, Perthshire. In this occurrence xenoliths of hornblendite and hornblende schist are enclosed in rocks of dioritic composition with small patches of appinites. He has shown that the later formed hornblendes show a definite decrease in the $Al_2O_3/Fe_2O_3$ ratio and an increase in the $MgO/FeO$ ratio. Deer further suggests that the higher the silica

content of the rock the higher should be the silica content of the hornblende. In the ensuing discussion it will be demonstrated that under the special conditions of granitization it may be possible for the silica content of hornblende to fall, simultaneously with the increase in silica content of the rock as a whole.
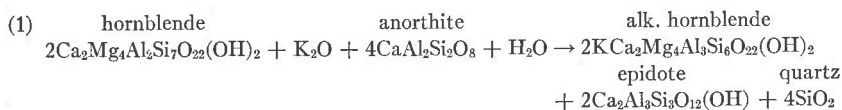
## THE GRANITIZATION OF HORNBLENDE ROCKS

The problem of granitization in the Piedmont of south-eastern Pennsylvania has been studied by several workers. The granitization of the Wissahickon formation in general has been discussed by Weiss (1949), and Ch'ih (1950) has dealt specifically with the chemistry of the granitization of the mica schists of this formation. Postel (1938, 1940) has described the granitization of hornblende gneisses associated with the Springfield granodiorite. Granitization of the schists is usually recognized by the appearance of potash minerals such as microcline and biotite. Of the granitization of the gabbroic rocks in the Baltimore gneiss there is little doubt, many of them showing migmatitic facies and distinct signs of assimilation by more felsic rocks.

With the analyses of several hornblendes from such grantized rocks it becomes possible to discuss the effect of granitization processes on this mineral; an aspect of the genesis of hornblende which has received little attention. Since almost all hornblende contains alkalies, which can be present in variable amounts, it is conceivable that the amount of potassium present should increase in hornblendes which have been granitized. An examination of the data in Table 3 shows that the number of potassium atoms in the vacant position AA′ is greatest in those hornblendes from rocks which are known to have been granitized (35-2, -10, -27). The granitization of the Van Artsdalen metagabbro (35-29) has been suggested (Weiss, 1947), and this would be in keeping with the high potash content. No direct reference has been made to the granitization of the metagabbro in the Marshalltown, Delaware area, whose hornblende is also potash rich.

A plot of the potassium atoms per unit cell versus the total sodium atoms per unit cell shows no regular arrangement of points. A plot of the number of potassium atoms per unit cell versus the sodium atoms in the vacant position, however, showed the hornblendes falling into two distinct groups. The hornblendes from rocks showing no obvious signs of granitization (35-5, -11, -22) as well as sample 35-29 fell along a straight line. All of the hornblendes known to be granitized as well as sample 35-31 fell in a group above this line. This suggests that the sodium which replaces the calcium represents an initial alkali content of the hornblende (small amounts of potassium may still be present in the vacant position),

and that further addition of alkalies, by whatever process, would introduce them into the vacant position. The ungranitized hornblendes falling on a line represent the addition of potassium and sodium in a certain ratio, the granitized hornblendes falling above this line represent the addition of these elements in a greater ratio to one another. In a true granitization process then, we should expect that the K/Na ratio should rise at the same time that the potassium content increases. Potassium content is plotted versus the ratio K/Na in the vacant position in Fig. 3. The hornblendes fall into two distinct groups. The granitized hornblendes show high potassium with a high K/Na ratio, while the ungranitized hornblendes show a low potassium with a low K/Na ratio.

In his discussion of the Springfield granodiorite Postel (1940) has pointed out several possible sources of granitizing solutions as proposed by earlier workers in this field. They are as follows: (*a*) the hydrolysis of the potash feldspar molecule at the end stages of crystallization to form muscovite and an alkali silicate liquid as shown by Goldschmidt (1922), (*b*) Eskola's (1932) hypothesis of a palingenetic granitic liquid which soaks up into the country rock, and (*c*) a pneumatolitic introduction of granitic material as suggested by MacGregor (1938). Although many more discussions of the origin of granitizing "solutions" are available, these three include the major possibilities. Any one of these processes could introduce potassium into the hornblendes. The following equation (1) illustrates the possible reaction between hornblende and an alkali silicate liquid:

(1)       hornblende            anorthite            alk. hornblende

$$2Ca_2Mg_4Al_2Si_7O_{22}(OH)_2 + K_2O + 4CaAl_2Si_2O_8 + H_2O \rightarrow 2KCa_2Mg_4Al_3Si_6O_{22}(OH)_2$$

$$\text{epidote} \qquad \text{quartz}$$
$$+ 2Ca_2Al_3Si_3O_{12}(OH) + 4SiO_2$$

Since the silica in the granitizing liquid does not take part in the reaction, it has not been included among the reactants. The anorthite is assumed to be present in the initial rock. This equation suggests a mechanism for the zoisitization of plagioclase. The next equation (2) shows the reaction between hornblende and feldspathic material to give an alkali hornblende and quartz:

(2)     $Ca_2Mg_4Al_2Si_7O_{22}(OH)_2 + KAlSi_3O_8 \rightarrow KCa_2Mg_4Al_3Si_6O_{22}(OH)_2 + 4SiO_2.$

No attempt is made to illustrate by equations the pneumatolitic introduction of potassium into hornblende.

From both equations it is seen that although silica is introduced, whether as alkali silicate or in a feldspar, the silica content of the hornblende decreases. Some compensation must be made for the introduction of alkali, and the correlation of alkali and aluminum content indicates that

this is accomplished by the replacement of silicon by aluminum. Such a process releases silica from the hornblende, which, together with the silica introduced would form quartz. It is possible, then, to decrease the silica content of the hornblende while the silica content of the rock as a whole increases. This is in contradiction with Deer's statement that the silica of hornblende and rock are proportional. The metagabbro in the vicinity of Marshalltown, Delaware (35-11), contains a large amount of quartz and potash-rich hornblende, which possibly illustrates the relationship discussed.

The only possible example of granitization by pneumatolitic processes encountered is the pargasitic hornblende from the metagabbro in the limestone at Van Artsdalen's quarry (35-29). The high fluorine content of the amphibole and the appearance of sodalite in the norms of the associated rocks (Weiss, 1947, p. 830) is suggestive of the influence of gaseous material. This hornblende falls just above the field of ungranitized horn-
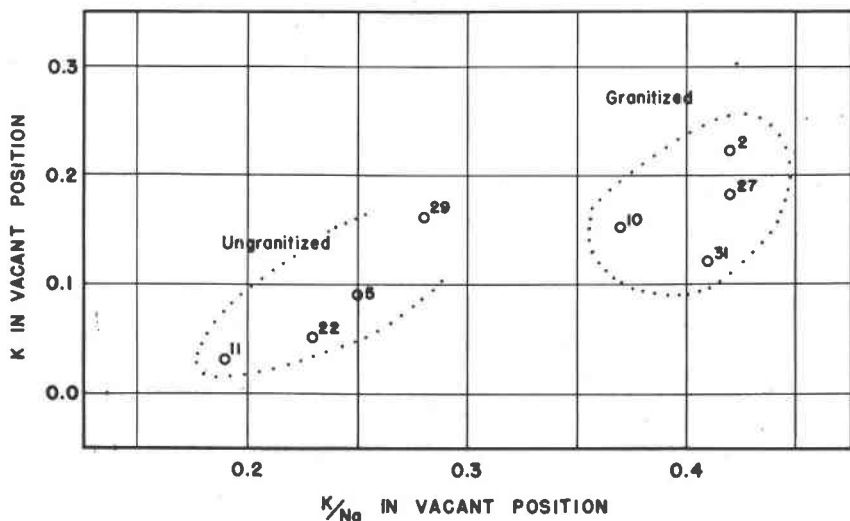


FIG. 3

blendes in Fig. 3, that is, it combines a high potassium content with a low K/Na ratio. It is clear that the process of introduction of potassium to this mineral is quite different from that of ordinary granitization. Pneumatolitic granitization might be expected to have different results from that effected by alkali silicate liquids.

The most interesting example of granitization of hornblendic rocks is that associated with the formation of the Springfield granodiorite. In this case the hornblende gneisses of the Wissahickon formation have been

converted to hornblende-biotite schists with the appearance of large amounts of epidote. The rock types have been described in detail by Postel (1938, 1940). The alkalization of hornblende is necessarily limited especially in the introduction of the large potassium ion, and hence the structure breaks down to form biotite. This conversion of hornblende to biotite is accompanied by the release of large amounts of lime, which must be accounted for. The only minerals into which the lime can go are epidote and sphene. While the sphene content of the rocks increases there is not enough titanium to handle even a major portion of the lime. The quantity of epidote rises locally to form a major portion of the rock and appears to be sufficient to account for all the lime. There is, however, a need for very large amounts of aluminum to form this mineral. Even if the granitizing material is assumed to be feldspathic, the alumina content is too low to combine with all of the lime released from the hornblende. It is possible that the lime freed from the hornblende migrates to those portions of the rock where appreciable anorthite is present and reacts with it to form epidote. This mechanism would account for the extremely high epidote content in some portions of the granitized hornblendic rocks.

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