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THE OPTICAL MINERALOGY, CHEMISTRY, AND X-RAY CRYSTALLOGRAPHY OF TEN CLINOPYROXENES FROM THE PENNSYLVANIA AND DELAWARE PIEDMONT PROVINCE

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ABSTRACT

Chemical, *x*-ray crystallographic, and optical properties of ten clinopyroxenes from rocks characteristic of the Pennsylvania and Delaware Piedmond Province have been determined and are reported in tabular form. Theoretical considerations and the presence of persistent unidentified reflections on diffractometer curves suggest that chemically complex clinopyroxenes are substructurally different from diopside. Differences between observed optical properties and properties predicted from chemical composition are due to differences between assumed and actual amounts of minor oxides present.

Geochemical relationships between clinopyroxenes and their coexisting orthopyroxene indicate that the samples studied here are of igneous origin. Subsequent metamorphism may have resulted in the introduction of Mg, the modification of pyroxene properties, and the establishment of equilibrium between pyroxene pairs.

INTRODUCTION

A study of the complex silicate minerals of the rocks of the Piedmont Province in Pennsylvania and Delaware was initiated by Rosenzweig's (1954) paper on hornblendes and Clavan's (1954) paper on hypersthenes. It was the purpose of these detailed mineralogical studies to compile for the complex silicates mentioned above optical, chemical and *x*-ray diffraction data, which at a later date could be coordinated with petrologic, structural and geochemical information, in the hope of throwing some light on the genesis and evolution of the metamorphic rocks which contained them.

This paper is a presentation of similar data for ten clinopyroxenes from the same metamorphic rocks. Optical, chemical and *x*-ray crystallographic properties have been determined and are tabulated. In addition to the presentation of detailed mineralogical information, geochemical ideas are advanced which, it is hoped, will contribute to a better understanding of the metamorphic rocks of the Piedmont Province.

GENERAL DESCRIPTION OF CLINOPYROXENE-BEARING ROCKS

The clinopyroxenes of this paper come from rock types which are typical of the Pennsylvania and Delaware Piedmont Province. In these

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metamorphic gabbros, norites, diorites and granites, it is rare that all three complex silicates, clinopyroxene, orthopyroxene, and hornblende, are present in quantities large enough for separation. Whenever possible, however, specimens which contained at least two of these were selected for study. A description of the samples chosen is given below. Table 1 gives volumetric analyses.

35-1N —Chester 16612.* Fine-grained massive gabbro xenolith in granite gneiss. Found as boulders in creek just north of Upper Bridge, Crum Creek Reservoir.

35-5N —West Chester 92755. Medium fine-grained hornblende norite showing faint foliation. Found as boulders in a field 300 yards west of road, 0.1 mile north of crossroads at Tallyville (Route 202). A part of the variable metagabbro body called the Wilmington gabbro.

TABLE 1. VOLUMETRIC ANALYSES

%	35-1N	35-5N	35-6N	35-8N	35-9N	35-13N	35-19N	35-24N	35-25N	35-32N
Clinopyroxene	21	9	7	9	23	16	23	3	18	16
Hypersthene	15	10	10	5	9	29	17	—	—	49
Hornblende	—	21	3	—	—	—	13	4	—	5
Plagioclase	An$_{52}$ 60	An$_{55}$ 55	An$_{56}$ 64	An$_{45}$ 56	An$_{55}$ 64	An$_{44}$ 44	An$_{75}$ 46	An$_{25}$ 11	An$_{26}$ 4	An$_{80}$ 28
Potash Feld.	—	—	—	—	—	—	—	Microcline 13	—	—
Quartz	—	—	10	26	—	—	—	66	26	—
Biotite	—	—	—	—	—	1	—	—	49	—
Garnet	—	—	—	—	—	6	—	—	—	—
Magnetite (plus Ilmenite)	4	5	5	3	4	4	<1	1	—	2
Serpentine	—	—	—	—	—	—	—	—	—	<1
Chlorite	—	<1	—	—	—	<1	—	—	—	—
Sphene	—	—	—	—	—	—	—	2	1	—
Apatite	<1	<1	<1	<1	<1	<1	—	—	1	—
Zircon	—	—	—	—	—	—	—	—	<1	—

35-6N —Wilmington 31268. Medium-grained massive quartz norite. Found in an outcrop in the park at Franklin and Sycamore Streets, Wilmington, Delaware. A part of the Wilmington gabbroic mass.

35-8N —Wilmington 32237. Fine-grained quartz-diorite. Found as the predominant rock type in the Alapocas Quarry on the east bank of Brandywine Creek in Wilmington, Delaware. A part of the Wilmington gabbroic mass.

35-9N —Wilmington 32237. Fine-grained massive gabbro. Found in the same quarry as 35-8N as dikes intrusive into quartz-diorite.

35-13N—Norristown 85826. Medium-grained hypersthene diorite. Found in the lower quarry wall on the west side of Radnor Quarry. A part of the Baltimore gneiss.

35-19N—West Chester 96413. Coarse-grained hornblende-eucrite. Found in boulders on the south side of Faulk Road, 1.5 miles northeast of the intersection of U. S. Route 202.

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* The numbers represent a grid index on the 15 minute quadrangle maps for the area.

35-24N—Chester 43216. Medium-grained granite gneiss. Found as the predominant rock type in the Lima Quarry. A part of the Lima granite gneiss.

35-25N—Chester 43216. Fine-grained quartz-diorite showing faint gneissic banding. Occurs as a xenolith in the Lima granite gneiss.

35-32N—Chester 22476. Coarse-grained eucritic norite. Found as boulders in a field 800 feet south of West Chester Pike at the Dinwoody Home. Part of an ultrabasic intrusion into the Wissahickon formation.

SAMPLE PREPARATION

Most of the pyroxenes used in this study had already been separated by Rosenzweig (1954) and Clavan (1954) in their studies of hornblendes and hypersthenes from southeastern Pennsylvania and Delaware, and details of separation have been given by Rosenzweig (1954). In cases where more clinopyroxene-separate was needed, or other clinopyroxene-bearing rocks were studied, Rosenzweig's separation scheme was followed.

In general, the rocks were crushed, using a small jaw crusher, a roller mill, and a ball mill, until they were fine enough to pass through a 100 mesh sieve. The 100 to 150 mesh portion was used for separation, particles of this size being for the most part monomineralic. Before separation was begun, however, this portion was wet screened on a 200 mesh sieve to remove dust and then rinsed with acetone and rapidly dried to avoid oxidation. Strongly magnetic particles were next removed with a hand magnet.

Because of the relatively large volumes of rock needed to obtain a sufficient amount of clinopyroxene-separate for chemical, optical, and *x*-ray determinations, the initial separation was accomplished using the Frantz isodynamic separator. In this way concentrates containing clinopyroxene, hornblende, and biotite were obtained and the final separation and purification was made using heavy liquids.

The purity of the clinopyroxene-separates obtained was tested by making grain counts on two balsam grain mounts of each sample. The samples range from 96.6% to 99.8% pure.

PRINCIPLES OF THE CHEMICAL ANALYSIS

Most of the elements were determined by the methods outlined in the previous paper (Clavan, 1954) and are not repeated here. These include: water, silica, ferrous oxide, chromic oxide, ferric oxide, aluminum oxide, titanium dioxide, manganous oxide and nickel oxide. In addition, the determination of specific gravity and the decomposition of the sample for determining many of the elements were carried out in the same way.

However, since these minerals are high in calcium and lower in magnesium and iron, the methods for calcium and magnesium had to be changed.

Also, since the time of the previous analyses, a new method was brought forth for the determination of potassium, which made the analyses for both potassium and sodium simpler and shorter.

The methods for calcium, magnesium, sodium, and potassium are outlined below.

PROCEDURE FOR THE CHEMICAL ANALYSIS

1. *Decomposition of the sample for the determination of sodium and potassium*

Weigh a 1 gram sample into a platinum dish and treat with 5 ml. of nitric acid, 10 ml. of perchloric acid and 10 ml. of hydrofluoric acid. Evaporate the solution to half the volume and add 10 ml. of hydrofluoric acid. Evaporate to fumes of perchloric acid and continue heating for 15 minutes. Cool the solution, transfer with water to a Pyrex beaker and evaporate to dryness. Bake the residue on a hot plate until no more fumes of perchloric acid are noted. Heat the sides of the beaker with a Bunsen burner to remove the last traces of perchloric acid.

Cool, add 50 ml. of a 10 per cent ammonium hydroxide solution and boil for 10 minutes. Filter and wash with 10 per cent ammonium hydroxide. Make the filtrate just acid with hydrochloric acid, cool, transfer to a 250 ml. volumetric flask and dilute to the mark.

2. *Sodium*

Pipet 100 ml. of the solution into a beaker, evaporate to dryness on the steam bath, add one ml. of water and 10 ml. of zinc uranyl acetate solution and stir well. Allow to stand one hour and filter on a weighed sintered glass crucible. Wash with small portions of the precipitating agent, five 2 ml. portions of ethyl alcohol saturated with the precipitate and finally with a small amount of acetone. Place the crucible in the balance case for 15 minutes and reweigh. The increase in weight is sodium zinc uranyl acetate with six molecules of water of crystallization and is calculated as sodium oxide.

3. *Potassium*

Pipet 100 ml. of the solution into a beaker and evaporate to dryness. Add 20 ml. of aqua regia and evaporate to dryness. Repeat with another 20 ml. of aqua regia. Dilute to 50 ml., add 2 ml. of hydrochloric acid and cool in ice. Add 25 ml. of a 1 per cent aqueous solution of sodium tetraphenyl boron which had been cooled to 0° C. Stir occasionally for 5 to 10 minutes while in the ice bath. Filter through a weighed sintered glass crucible and wash with 3–10 ml. portions of a freshly prepared saturated solution of potassium tetraphenyl boron. Dry at 100° C. for one hour and reweigh. Calculate as potassium oxide

4. *Calcium*

Pipet a 100 ml. aliquot from the 500 ml. volumetric flask (which contains 2 grams of sample decomposed by hydrofluoric and perchloric acids) into a beaker and dilute to 250 ml. Add 2 grams of ammonium chloride, heat the solution almost to boiling and add ammonium hydroxide until it is just alkaline to litmus. Add 5 ml. of saturated bromine water, test the solution to make sure it is still ammoniacal and boil for 15 minutes. Filter the precipitate while the solution is still hot, wash well with a 3 per cent ammonium chloride solution, dissolve the precipitate off the paper with hot dilute hydrochloric acid and reprecipitate as above. Discard the precipitate and combine the filtrates. Reduce the volume of the filtrates to 250 ml., add 2 grams of ammonium oxalate and then add hydrochloric acid until the precipitate dissolves. Heat the solution almost to boiling, add 2 drops of methyl red indicator and ammonium hydroxide until the solution is just alkaline. Place on the steam bath overnight.

Cool, filter and wash with a 3 per cent ammonium oxalate solution. Save the filtrate. Dissolve the precipitate off the paper with hot dilute hydrochloric acid and reprecipitate as above. Combine the filtrates and save for the determination of magnesium. Place the precipitate in a weighed platinum crucible, dry, ignite over 950° C., cool and reweigh. The increase in weight is calcium oxide.

5. *Magnesium*

Reduce the volume of the combined filtrates from the determination of calcium to 250 ml. Make just acid with hydrochloric acid and add 0.5 grams of diammonium hydrogen phosphate. Cool to below room temperature, add ammonium hydroxide dropwise until the solution is just basic, allow the magnesium to precipitate and then add an excess of 30 ml. of ammonium hydroxide. Stir the solution occasionally during the next 30 minutes and allow to stand overnight. Filter the precipitate through paper, wash with 1:20 ammonium hydroxide, dissolve off the paper with 1:10 hydrochloric acid and reprecipitate as above. Filter this precipitate through a weighed porcelain filtering crucible, wash with 1:20 ammonium hydroxide, dry and ignite for one hour. Cool and reweigh as magnesium pyrophosphate. Calculate as magnesium oxide.

CHEMICAL DATA

The chemical compositions and specific gravities of the clinopyroxenes studied here are reported in Table 2. SiO_2 is high and fairly constant. Other major constituents, CaO, MgO, FeO, are variable. Variability is also shown by the minor constituents, especially Al_2O_3, Fe_2O_3, Na_2O, TiO_2, and MnO. Specific gravities range from 3.303 to 3.420 and are roughly related to mole per cent ferrous silicate (Fig. 1). In order to facilitate chemical and petrological calculations, weight per cents were converted to atomic ratios in Tables 5–14.

The theoretical formula for clinopyroxene (Berman, 1937) is W (X, Y) Z_2O_6, four such units belonging to a unit cell. In all cases the major W,

TABLE 2. CHEMICAL ANALYSES AND SPECIFIC GRAVITIES

	35-1N	35-5N	35-6N	35-8N	35-9N	35-13N	35-19N	35-24N	35-25N	35-32N
SiO_2	52.67	51.03	51.00	50.17	51.55	50.95	51.43	50.77	52.37	50.00
Al_2O_3	1.42	2.40	2.49	2.38	2.44	3.49	2.63	1.65	1.38	3.05
Fe_2O_3	1.23	1.88	2.03	3.39	2.03	1.40	1.70	4.46	3.32	1.50
FeO	4.34	8.97	9.31	8.05	7.28	9.52	5.92	8.69	7.02	5.87
MgO	15.59	13.11	12.53	13.22	13.65	12.22	14.83	10.14	12.59	15.60
CaO	23.81	21.75	21.08	21.10	21.73	20.55	22.18	20.70	21.46	22.42
Na_2O	0.45	0.43	0.47	0.49	0.52	0.70	0.44	1.41	1.19	0.18
K_2O	0.00	0.00	0.00	0.00	0.00	0.24	0.00	0.14	0.24	0.00
H_2O	0.20	0.24	0.37	0.18	0.26	0.24	0.31	0.22	0.18	0.27
TiO_2	0.14	0.28	0.27	0.28	0.31	0.36	0.28	0.28	0.19	0.40
Cr_2O_3	0.00	0.00	0.00	0.00	0.01	0.06	0.04	0.01	0.05	0.07
NiO	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.03
MnO	0.13	0.35	0.45	0.34	0.24	0.19	0.19	1.35	0.46	0.18
Total	99.98	100.45	100.01	99.61	100.03	99.93	99.96	99.83	100.47	99.57
Sp.Gr.	3.303	3.384	3.385	3.382	3.358	3.364	3.332	3.420	3.364	3.324

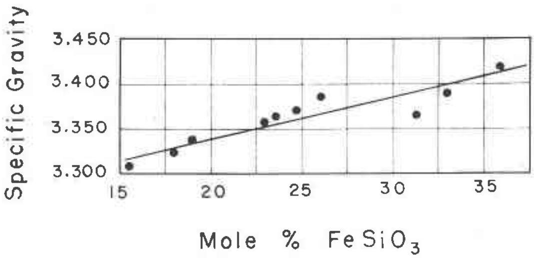

FIG. 1. Relation between specific gravity and mole per cent ferrous silicate.

X and Y ions are Ca^{+2}, Mg^{+2}, and Fe^{+2} respectively, but limited substitution usually takes place. In general:

W = Ca^{+2}, Na^{+1}
X = Mg^{+2}, Fe^{+2}, Mn^{+2}, Ni^{+2}
Y = Al^{+3}, Fe^{+3}, Cr^{+3}, Ti^{+4}
Z = Si^{+4}, Al^{+3}

In some of the possible substitutions listed (Na^{+1} for Ca^{+2}, Ti^{+4} for Al^{+3}, Al^{+3} for Si^{+4}, and elements of the Y group for X) electrical neutrality will not be maintained unless there is a distribution of substituting ions so that their charges will balance one another. The number of ions going into each group must satisfy (*a*) the electrical requirement that the -12 charge of the six O^{-2} ions is neutralized by the sum of the ionic charges in the W, X, Y, Z groups, and (*b*) the structural requirement that each of the (W) and (X, Y) groups, which have coordinations of 8 and 6 respectively, must contain two ions.

Steps for determining the correct proportion of ions in each group given by Hess (1949) were followed. Each of these steps corresponds to a column in Tables 5–14.

1. Na and Cr ions are combined (1:1) to make $NaCrSi_2O_6$. If K ions are present, they are united with Na ions.
    a. If Na is in excess of Cr, see steps 2 and 3.
    b. If Cr is in excess of Na, see step 5.
2. If some Na ions are left over, they are combined with Fe^{+3} ions (1:1) to make $NaFeSi_2O_6$.
    a. If Na is in excess of Fe^{+3}, see step 3.
    b. If Fe^{+3} is in excess of Na, see step 6.
3. If there are still some Na ions left, they are combined (1:1) with Al ions to make $NaAlSi_2O_6$.
4. Ti ions are combined with Al ions (1:2).
5. Cr ions are combined with Al ions (1:1).

6. Fe^{+3} ions are combined with Al ions (1:1).
7. Of the remaining Al ions, one-half is allotted to each of the Y and Z groups.

From the theoretical formula it can be seen that the ratio of cations to oxygen is 2:2:6. Hence if the chemical analysis is accurate and the sample pure, (a) the total number of ions in the Z group will theoretically equal the total number of ions in the W and (X, Y) groups, and (b) the ratio of (W, X, Y) and Z to the total number of O^{-2} ions will be 2:2:6. This is tested by first dividing the total number of oxygens by six, and then dividing the resulting figure into the total number of ions in Z and (W, X, Y) respectively. If the analysis is satisfactory,* the result of these divisions will equal 2.00±.02. The columns entitled "Cations to Six O" in Tables 5–14 show the results of this test. It can be seen that all the analyses are quite satisfactory with the possible exception of 35-32N. Although this sample is the purest, 99.8%, it appears to have the greatest deviation, +.07. The large deviation of +.06 in the case of 35-6N is explained by the fact that this sample is least pure, 96.6%.

Ca:Mg:Fe ratios have been calculated and are given in Tables 5–14. The procedure of Hess is again followed, so that in this calculation Fe^{+2} and Mn are added to Fe^{+3}, and Ni is added to Mg. The amount of Al replacing Si in the chains is given below the Ca:Mg:Fe ratios.

X-RAY DIFFRACTION DATA

X-ray diffractometer curves for each sample were obtained using a wide range Philips geiger counter *x*-ray diffractometer with filtered copper K radiation.† Samples were scanned at the rate of 1° per minute, and for all runs the scaler was set at 2×, the multiplier at 0.6, and the time constant at 8. Table 3 is a representative example of the *d*-spacings and relative intensities of peaks calculated from these curves.

Indices were determined by comparing observed $\sin^2 \theta$ values with $\sin^2 \theta$ values calculated from the theoretical formula for a monoclinic unit cell using the cell dimensions and axial angle determined by Warren and Bragg (1928) for diopside.

The calculation of $\sin^2 \theta$ values for planes satisfying the space group conditions ($C_{2h}{}^6$) was performed on an IBM 602A computer. The indices of reflections for the clinopyroxenes were obtained by comparison of calculated $\sin^2 \theta$ values with $\sin^2 \theta$ values obtained from 2θ readings taken from the spectrometer curves. Where good agreement was found, the indices used to determine the calculated $\sin^2 \theta$ values were assigned to the observed reflection.

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* A satisfactory silicate analysis is accurate to 2%.

† 40 KV at 17 MA.

TABLE 3. EXAMPLE OF *d*-SPACINGS AND SPECIFIC GRAVITIES
Sample 35-1N

d (Å)	I/I$_0$	*d* (Å)	I/I$_0$
3.332	5	1.589	5
3.229	95	1.550	10
3.115	5	1.525	5
2.991	100	1.503	5
2.949	85	1.485	5
2.891	30	1.422	10
2.568	10	1.408	5
2.518	40	1.386	5
2.302	10	1.374	5
2.206	5	1.328	10
2.149	20	1.282	5
2.132	25	1.265	5
2.108	15	1.248	5
2.036	10	1.212	5
2.014	5	1.196	5
1.859	5	1.173	5
1.836	10	1.0745	10
1.772	5	1.0718	10
1.754	10	1.0690	10
1.674	5	1.0640	5
1.650	10	1.0418	5
1.624	20	1.0298	5
1.620	20	1.0183	5

Figure 2 shows the actual relationship between twice an angle (2θ) and the sine of the angle squared ($\sin^2 \theta$). Figure 3 is based on this relationship, and indicates the amount of deviation of 2θ for various portions of the $2\theta-\sin^2 \theta$ curve (Fig. 2) corresponding to a deviation in calculated and observed $\sin^2 \theta$ values. Taking into account minor shifts of peaks, the maximum $\Delta 2\theta$ acceptable here for a spectrometer chart running at the rate of 1° per minute is 0.3°. Hence the agreement between calculated and observed $\sin^2 \theta$ values may be tested by finding the difference between them ($\Delta\sin^2\theta \times 10^{-4}$) and then using the curves of Fig. 3 to find the corresponding $\Delta 2\theta$. If $\Delta 2\theta$ is less than 0.3°, the reflection is given the indices from which the calculated $\sin^2\theta$ value was derived.

OPTICAL DATA

With few exceptions the methods for determination of the optical properties of clinopyroxenes given by Hess (1949) were used in this investigation. In order to facilitate comparison of the optical and chemical properties of the clinopyroxenes of this study with those of the clino-

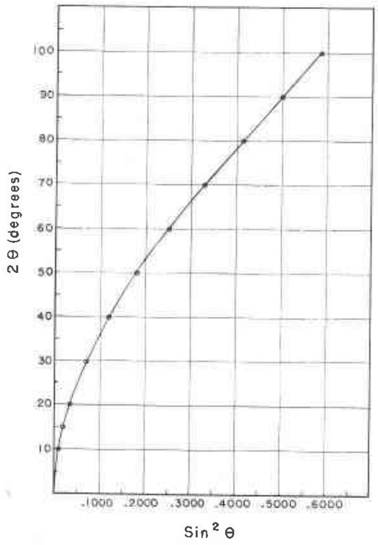


FIG. 2. Relation between twice an angle and the sine of the angle squared.

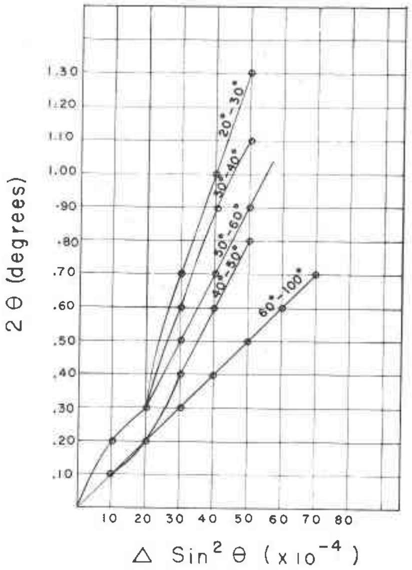


FIG. 3. Relation between 2θ and $\sin^2\theta$.

pyroxenes studied by Hess, his basic form of reporting these values has been followed (Tables 24–33).

Optic Angle

Optic angle determinations were made using a four-axis universal stage. Grains were selected whose optic plane could be made vertical, and 2V was measured directly by rotation from one "optic eye" to the other. The 2V values were corrected for the refractive index of the hemispheres and for the Y-index of the particular clinoypyroxene being measured.

Refractive Indices

Of the indices given for each clinopyroxene only the Y index actually has been measured, X and Z having been calculated from birefringence and optic angle values. {100} parting tablets were used for the determination of Y. These are recognized by their low birefringence, and, if bounded by cleavage planes, by parallel extinction. In such grains the optic plane is upright and an optic axis emerges about 20° from the vertical, hence an off-center optic axis figure will be obtained in convergent light. When the isogyre is rotated to the E-W position, Y, the optic normal is N-S, and the grain is in the proper orientation to determine the X-index.

All refractive index measurements were made in white light at 25° C. Each clinopyroxene was first bracketed between two liquids whose refractive indices were .001 apart. Liquids at intervals of .0002 within these groups were prepared as needed, using a Pulfrich refractometer with a sodium light and constant temperature (25° C.), thus giving the final Y-index value to ±.0001.

Extinction Angle, $Z \wedge C$

The clinopyroxenes of this study did not show twinning or exsolution lamellae, therefore neither of the methods suggested by Hess (1949) for the determination of $Z \wedge C$ could be used. However, two other methods, both of which give results consistent within ±2° were used.

A. *Cleavage Method*

Since the precise measurement of $Z \wedge C$ depends on the exact orientation of the clinopyroxene so that {010} is horizontal, the biggest problem is the recognition of grains in which this condition obtains. Grains which lie in this approximate orientation can be recognized by their high birefringence, the birefringence on {010} being the maximum. If the grain should happen to have the {010} direction exactly horizontal, the {110} cleavages will make an angle of 46.5° with vertical, since for clinopyroxene the cleavage angle facing {010} is 93°. Furthermore, in grains in which two sets of cleavages are developed, these will be seen to dip inward at equal angles in opposite directions. Should the clinopyroxene grain be ground so that the surface which is horizontal lies between the {010} and {110} directions, the angle which one of the {110} cleavages makes with vertical will be less than 46.5°, while the angle which the {110} cleavage makes will be greater than 46.5°, the minimum or maximum respectively being reached when the {110} direction is horizontal.

Hence, if a universal stage is used, it is possible to orient grains of clinopyroxene so that their {010} direction is horizontal. This is done in the following way:

1. A grain is located which lies with {010} approximately horizontal. Such a grain may be recognized by its high birefringence, as mentioned above, and by the fact that the cleavage or cleavages will appear broad. The grain is placed so that its cleavage is parallel to the H or the K axis.
2. The height of the thin section is adjusted so that the plane of a selected cleavage will contain either the H or K axis of rotation of the U-stage. This condition obtains when cross hair (N-S for H, E-W for K) seems to lie in the cleavage plane throughout a rotation about H or K.
3. The angle which the cleavage makes with vertical (θ) is measured by rotating the cleavage plane on either H or K until it stands vertical. When the cleavage plane is vertical, it will appear as a sharp, well-defined line.

4. Since θ represents the angle between a cleavage plane and vertical, it also represents the angle of dip of the cleavage plane when the thin section is horizontal. Hence, if the cleavage plane is counter-rotated by an amount $46.5°-\theta$, the {010} direction will be made horizontal.

Once the {010} direction has been made horizontal, $Z \wedge C$ is measured in the usual way.

B. [001] *Zone Method*

In some of the clinopyroxenes studied, {110} cleavage was absent or poorly developed. In such cases extinction angles were measured in the zone [001], the maximum extinction angle being that on {010}. The zone [001] is recognized by the general shape of grains and by the fact that the other two cleavages {100} and {010} also lie in this zone. Grains which have {010} nearly horizontal can be recognized by their high birofringence.

A comparison of the extinction angles obtained by the two methods is given below for 35-1N (Table 4).

TABLE 4. COMPARISON OF RESULTS FROM CLEAVAGE AND ZONE METHODS OF EXTINCTION ANGLE MEASUREMENTS

Cleavage Method	Zone Method
37.3	37.3
38.0	37.3
38.6	37.6
38.7	38.6
	38.8

Birefringence

Since the maximum birefringence in clinopyroxene is seen when {010} is horizontal, one of the procedures outlined above was used to orient grains for birefringence measurements. Determinations were made using a Berek compensator with the aid of special slides which are prepared as follows: A mixture of equal parts of clinopyroxene and quartz (crushed to approximately the same size) is poured into a Buehler mount cylinder to form a layer one grain thick on the cylinder bottom. Next, about 3–4 cc. of Transoptic mounting powder is loaded into the cylinder on top of the clinopyroxene-quartz layer, and the piston introduced. The cylinder thus loaded is placed in a Buehler press and subjected to a pressure of 5000 psi.

The surface of the grain mounts containing the clinopyroxene-quartz layer is semi-polished on a lap until the grains show relief and have flat surfaces. The semi-polished surface is cemented to a glass slide using liquid balsam, and the mount is ground as thin as possible, using a grinding wheel. Further grinding is accomplished with a fine-grade abrasive paper, and grinding is continued until the clinopyroxene-quartz layer is approximately .04 mm. thick, and until the grains show relief and have flat surfaces. The surface is then semi-polished and covered with a cover glass, using liquid balsam.

The method of slide preparation described above insures as nearly as possible the coplanar distribution of clinopyroxene and quartz grains. In making actual retardation measurements, grains not having flat surfaces should be avoided, as such grains will give a retardation for a thickness which is less than the true thickness of the slide at that particular point.

After the {010} retardation of a clinopyroxene grain has been measured, the thickness at this point is determined by measuring the retardation of several neighboring quartz grains. The quartz grains chosen for this purpose must be capable of having their *c*-axis rotated into a horizontal position so that maximum birefringence is obtained. Since the birefringence of quartz is known, retardation can be directly converted to thickness. This thickness value, of course, must be corrected for the angle of tilt of the universal stage. Since in most cases a double tilt was required to make the *c*-axis horizontal, the thickness was corrected by multiplying by the cosine of the angle between the microscope axis and the perpendicular to the inner stage. This angle is obtained by reference to plate 9 in Emmons (1943). The thickness is further corrected by dividing by the cosine of the angle of tilt necessary to make clinopyroxene {010} planes horizontal. Curves given in Winchell (1929) convert the doubly corrected thickness and the retardation values to birefringences.

CHEMICAL CRYSTALLOGRAPHY

The clinopyroxenes studied here gave a number of reflections whose $\sin^2\theta$ values did not agree well enough with calculated $\sin^2\theta$ values to be assigned indices. A number of unidentified lines were also observed by Kuno and Hess (1935) in their paper on the unit cell dimensions of clinoenstatite and pigeonite. Since they obtained excellent agreement between their *d*-spacings and *d*-spacings calculated from their unit cell dimensions, and since the number of unidentified lines was few and their intensities weak, they concluded that the unidentified reflections were due to sample impurity, and that all clinopyroxenes have the same structure as diopide.

One of the unidentified reflections observed in the present study appeared consistently in all the diffraction patterns with the exception of

TABLE 5. 35-1N

Diopside. Chester 14373.
Upper Bridge. Crum Creek Reservoir.

	Wt. %	Atomic Ratios		1	2	3	4	5	6	7		Cat-ions to Six O
				Cr Na	Fe''' Na	Al Na	2Al Ti	Al Cr	Al Fe'''	Al Al	Z Y W	
SiO_2	52.67	Si	876								Z	
Al_2O_3	1.42											
Fe_2O_3	1.23	Al	28				4		½	11½	892	1.98
FeO	4.34									12		
MgO	15.59	Fe'''	15		14½				½			
CaO	23.81	Cr	0									
Na_2O	0.45	Fe	60									
K_2O	0.00	Mn	2								WXY	2.03
H_2O	0.20	Ni	0								917	
TiO_2	0.14	Mg	386½									
Cr_2O_3	0.00	Ca	425									
MnO	0.13	Na	14½		14½							
NiO	0.00	K	0									
		Ti	2				2					
	99.98	O	2702									

Specific Gravity: 3.303

$Ca_{47.8}\ Mg_{43.5}\ Fe_{8.7}$
% Al in Z = 1.8

Indices of Refraction
nX 1.6791
nY 1.6843
nZ 1.7071

Pleochroism:
Nonpleochroic
Colorless

Birefringence, x10^4 aver.: 280

262, 270, 272, 290, 308

2V aver.: **50½°**

44½°, 43 3/4°, 50°, 51 3/4°,
52°, 52°, 52 3/4°, 53½°, 55¼°

Z∧C aver.: 38°

37°, 37¼°, 37¼°, 37¼°, 37½°,
38°, 38¼°, 38½°, 38½°, 38 3/4°,
38 3/4°

Sample purity: 98.6%

TABLE 6. 35-5N

Augite. West Chester. 92755. Tallyville.

		Atomic Ratios		1	2	3	4	5	6	7		Cat-ions to Six O
				Cr Na	Fe''' Na	Al Na	2Al Ti	Al Cr	Al Fe'''	Al Al	Z Y W	
SiO_2	51.03	Si	849								Z	
Al_2O_3	2.40										881	1.99
Fe_2O_3	1.88	Al	47				7		10	15		
FeO	8.97									15		
MgO	13.11	Fe'''	24		14				10			
CaO	21.75	Cr	0									
Na_2O_3	0.43	Fe	125									
K_2O	0.00	Mn	5								WXY	2.02
H_2O	0.24	Ni	0.1								899½	
TiO_2	0.28	Mg	325									
Cr_2O_3	0.00	Ca	388									
MnO	0.35	Na	14		14							
NiO	0.01	K	0									
		Ti	3½				3½					
	100.45	O	2661									

Specific Gravity: 3.384

$Ca_{44.7}\ Mg_{37.5}\ Fe_{17.8}$
% Al in Z = 3.6

Indices of Refraction
nX 1.6868
nY 1.6908
nZ 1.7125

Pleochroism:
Faintly pleochroic
in green.

Birefringence, x10^4 aver. 257

240, 245, 249,
271, 279

2V aver.: 46½°

44°, 44 3/4°, 45°, 45¼°,
45 3/4°, 45 3/4°, 46¼°, 48¼°,
48 3/4°, 48 3/4°, 50¼°

Z∧c aver.: 43°

41°, 42°, 42½°, 42 3/4°,
43½°, 43½°, 44½°, 44 3/4°

Sample purity: 99.3%

TABLE 7. 35-6N

Augite. Wilmington 31268. Wilmington, Delaware.

				1	2	3	4	5	6	7		
		Atomic Ratios					2Al	Al	Al	Al	Z	Cations to Six O
				Cr	Fe'''	Al	Ti	Cr	Fe'''	Al	Y	
				Na	Na	Na					W	
SiO_2	51.00	Si	835								Z 867½	1.99
Al_2O_3	2.49											
Fe_2O_3	2.03	Al	49				6		10½	16 16½		
FeO	9.31											
MgO	12.53	Fe'''	25½		15				10½			
CaO	21.08	Cr	0									
Na_2O	0.47	Fe	129½									
K_2O	0.00	Mn	6									
H_2O	0.37	Ni	0.1								WXY 898½	2.06
TiO_2	0.27	Mg	311									
Cr_2O_3	00.00	Ca	376									
MnO	0.45	Na	15		15		3					
NiO	0.01	K	0									
		Ti	3									
	100.01	O	2618									

Specific Gravity: 3.385

$Ca_{44.3}\ Mg_{36.7}\ Fe_{19.0}$

% Al in Z = 3.7

Indices of Refraction
nX 1.6918
nY 1.6959
nZ 1.7210

Pleochroism:
Faintly pleochroic in green.

Birefringence, x10^4 aver.: 292

269, 296, 299, 304

2V aver.: 43 3/4°

41½°, 43°, 43 3/4°, 44°, 44¼°, 44¼°, 44½°, 45¼°

Z∧c aver.: 40½°

39½°, 39 3/4°, 40°, 40°, 40½°, 41½°, 42 3/4°

Sample purity: 96.6%

TABLE 8. 35-8N

Augite. Wilmington 32237. Wilmington, Delaware.

				1	2	3	4	5	6	7		
		Atomic Ratios					2Al	Al	Al	Al	Z	Cations to Six O
				Cr	Fe'''	Al	Ti	Cr	Fe'''	Al	Y	
				Na	Na	Na					W	
SiO_2	50.17	Si	835								Z 875½	1.99
Al_2O_3	2.38											
Fe_2O_3	3.39	Al	47				7		27	6½ 6½		
FeO	8.05											
MgO	13.22	Fe'''	43		16				27			
CaO	21.10	Cr	0									
Na_2O	0.49	Fe	112									
K_2O	0.00	Mn	5									
H_2O	0.18	Ni	0.1								WXY 890½	2.02
TiO_2	0.28	Mg	328									
Cr_2O_3	0.00	Ca	376½									
MnO	0.34	Na	16		16							
NiO	0.01	K	0									
		Ti	3½				3½					
	99.61	O	2640									

Specific Gravity: 3.382

$Ca_{43.5}\ Mg_{38.0}\ Fe_{18.5}$

% Al in Z = 4.6

Indices of Refraction
nX 1.6865
nY 1.6909
nZ 1.7119

Pleochroism:
Nonpleochroic
Color: green

Birefringence, x10^4 aver.: 254

244, 254, 264

2V aver.: 50¼°

49°, 49¼°, 50¼°, 50½°, 51½°, 54¼°

Z∧c aver.: 42°

40½°, 41 3/4°, 42°, 43¼°

Sample purity: 97.9%

TABLE 9. 35-9N

Salite. Wilmington 32237. Wilmington, Delaware.

		Atomic Ratios		1	2	3	4	5	6	7		
							2Al	Al	Al	Al	Z	Cat-ions
				Cr	Fe'''	Al	Ti	Cr	Fe'''	Al	Y	to
				Na	Na	Na					W	Six O
SiO_2	51.55	Si	858								Z	
Al_2O_3	2.44										890	1.99
Fe_2O_3	2.03	Al	48				8		8	16		
FeO	7.28									16		
MgO	13.65	Fe'''	25		17				8			
CaO	21.73	Cr	0.1									
Na_2O_3	0.52	Fe	101									
K_2O	0.00	Mn	3								WXY	2.00
H_2O	0.26	Ni	0.1								892	
TiO_2	0.31	Mg	338									
Cr_2O_3	0.01	Ca	388									
MnO	0.24	Na	17		17							
NiO	0.01	K	0									
		Ti	4				4					
	100.03	O	2673									

Specific Gravity: 3.358

$Ca_{45.4}\ Mg_{39.6}\ Fe_{15.1}$
% Al in Z = 3.6

Indices of Refraction
nX 1.6911
nY 1.6951
nZ 1.7167

Pleochroism:
Nonpleochroic
Color: green

Birefringence, x10^4 aver. 256

233, 266, 269

2V aver.: 46 3/4°

42 3/4°, 44 3/4°, 44 3/4°, 45°, 45 3/4°, 46½°, 47°, 48°, 51 3/4°, 52¼°

Z∧c aver.: 39½°

38°, 38 3/4°, 39°, 39¼°, 40°, 40°, 40½°, 40 3/4°

Sample purity: 98.4%

TABLE 10. 35-13N

Augite. Norristown 85826. Radnor Quarry.

		Atomic Ratios		1	2	3	4	5	6	7		
							2Al	Al	Al	Al	Z	Cat-ions
				Cr	Fe'''	Al	Ti	Cr	Fe'''	Al	Y	to
				Na	Na	Na					W	Six O
SiO_2	50.95	Si	846								Z	
Al_2O_3	3.49					11¼	9			24¾	891	2.02
Fe_2O_3	1.40	Al	69									
FeO	9.52									25		
MgO	12.22	Fe'''	17½		17½							
CaO	20.55	Cr	3/4	3/4								
Na_2O	0.70	Fe	132½									
K_2O	0.24	Mn	3								WXY	
H_2O	0.24	Ni	0.1									
TiO_2	0.36	Mg	303								880¾	1.99
Cr_2O_3	0.06	Ca	366½									
MnO	0.19	Na	23	3/4	11¼	11¼						
NiO	0.01	K	5		5							
		Ti	4½				4½					
	99.93	O	2651									

Specific Gravity: 3.364

$Ca_{44.6}\ Mg_{36.8}\ Fe_{18.6}$
% Al in Z = 5.1

Indices of Refraction
nX 1.6858
nY 1.6905
nZ 1.7139

Pleochroism:
Nonpleochroic
Color: green

Birefringence, x10^4 aver.: 281

265, 280, 281, 298

2V aver.: 48°

43½°, 45¼°, 46¼°, 48½°, 48 3/4°, 48 3/4°, 48 3/4°, 51¼°, 51 3/4°

Z∧c aver.: 41°

40°, 40°, 40¼°, 41¼°, 41¼°, 41½°, 42¼°

Sample purity: 98.3%

TABLE 11. 35-19N

Salite. West Chester 96413.

		Atomic Ratios		1 Cr Na	2 Fe''' Na	3 Al Na	4 2Al Ti	5 Al Cr	6 Al Fe'''	7 Al Al	Z Y W	Cat-ions to Six O
SiO_2	51.43	Si	856								Z	
Al_2O_3	2.63											
Fe_2O_3	1.70	Al	52				7		7½	18½ 19	889	1.99
FeO	5.92											
MgO	14.83	Fe'''	21		13½				7½			
CaO	22.18	Cr	½	½								
Na_2O	0.44	Fe	82									
K_2O	0.00	Mn	3								WXY	
H_2O	0.31	Ni	0.1								907	2.03
TiO_2	0.28	Mg	368									
Cr_2O_3	0.04	Ca	396									
MnO	0.19	Na	14	½	13½							
NiO	0.01	K	0									
		Ti	3½				3½					
	99.96	O	2685									

Specific Gravity: 3.332

$Ca_{45.5}$ $Mg_{42.3}$ $Fe_{12.2}$
% Al in Z = 3.7

Indices of Refraction

nX	1.6862
nY	1.6908
nZ	1.7141

Pleochroism:

Nonpleochroic
Color: Faint green

Birefringence x10^4 aver.: 279

265, 269, 274, 284, 305

2V aver.: 48°

44 3/4°, 44 3/4°, 45 3/4°, 47¼°, 48°, 48°, 48 3/4°, 50¼°, 50 3/4°, 51¼°

Z∧c aver.: 39¼°

37°, 37 3/4°, 38°, 38 3/4°, 39°, 39 3/4°, 40°, 40°, 40°, 41¼°, 41½°

Sample purity: 98.8%

TABLE 12. 35-24N

Salite. Chester 43216. Lima Quarry.

		Atomic Ratios		1 Cr Na	2 Fe''' Na	3 Al Na	4 2Al Ti	5 Al Cr	6 Al Fe'''	7 Al Al	Z Y W	Cat-ions to Six O
SiO_2	50.77	Si	845								Z	
Al_2O_3	1.65						7		7½	8½ 9	868	2.00
Fe_2O_3	4.46	Al	32									
FeO	8.69											
MgO	10.14	Fe'''	56		48½				7½			
CaO	20.70	Cr	0.1									
Na_2O	1.41	Fe	121									
K_2O	0.14	Mn	19								WXY	
H_2O	0.22	Ni	0.1								877	2.02
TiO_2	0.28	Mg	251									
Cr_2O_3	0.01	Ca	369									
MnO	1.35	Na	45½		45½ 3							
NiO	0.01	K	3									
		Ti	3½				3½					
	99.83	O	2613									

Specific Gravity: 3.420

$Ca_{45.2}$ $Mg_{30.8}$ $Fe_{24.0}$
% Al in Z = 2.6

Indices of Refraction

nX	1.6972
nY	1.7029
nZ	1.7215

Pleochroism:

Faintly pleochroic
Color: Vivid green

Birefringence,x10^4 aver.: 243

237, 237, 239, 258

2V aver.: 57 3/4°

55°, 56½°, 57°, 57°, 57¼°, 58°, 58 3/4°, 59°, 59½°, 60°

Z∧c aver.: 42½°

40°, 40°, 42°, 42°, 42°, 44°, 44°, 44°, 44 3/4°

Sample purity: 98.9%

TABLE 13. 35-25N

Salite. Chester 43216. Lima Quarry.

SiO_2	52.37
Al_2O_3	1.38
Fe_2O_3	3.32
FeO	7.02
MgO	12.59
CaO	21.46
Na_2O	1.19
K_2O	0.24
H_2O	0.18
TiO_2	0.19
Cr_2O_3	0.05
MnO	0.46
NiO	0.02
	100.47

		1	2	3	4	5	6	7		
					2Al	Al	Al	Al	Z	Cat-ions
Atomic Ratios		Cr	Fe'''	Al	Ti	Cr	Fe'''	Al	Y	to
		Na	Na	Na					W	Six O
Si	871								Z 887	1.99
Al	27			1	4			11 11		
Fe'''	41½		41½							
Cr	½	½								
Fe	98									
Mn	6½								WXY 897¾	2.02
Ni	0.3									
Mg	312									
Ca	383									
Na	38	½	36½	1						
K	5		5							
Ti	2				2					
O	2672									

Specific Gravity: 3.364

$Ca_{45.5}$ $Mg_{37.1}$ $Fe_{17.4}$

% Al in Z = 1.8

Indices of Refraction
nX 1.6937
nY 1.6983
nZ 1.7157

Pleochroism:
Faintly Pleochroic
Color: Vivid green

Birefringence, x10^4 aver.: 220

212, 212, 222, 234

2V aver.: 54¼°

51¼°, 51½°, 51 3/4°, 52¼°, 53¼°, 53¼°, 54°, 54¼°, 54 3/4°, 55°, 56°, 56 3/4°, 61°

Z∧c aver.: 39¼°

38½°, 39°, 39¼°, 39½°, 39½°

Sample purity: 99.5%

TABLE 14. 35-32N

Augite. Chester. 22476.

SiO_2	50.00
Al_2O_3	3.05
Fe_2O_3	1.50
FeO	5.87
MgO	15.60
CaO	22.42
Na_2O	0.18
K_2O	0.00
H_2O	0.27
TiO_2	0.40
Cr_2O_3	0.07
MnO	0.18
NiO	0.03
	99.57

		1	2	3	4	5	6	7		
					2Al	Al	Al	Al	Z	Cat-ions
Atomic Ratios		Cr	Fe'''	Al	Ti	Cr	Fe'''	Al	Y	to
		Na	Na	Na					W	Six O
Si	832								Z 873½	1.97
Al	60				10		13½	18 18½		
Fe'''	19		5½				13½			
Cr	½	½								
Fe	82									
Mn	2½								WXY 921	2.07
Ni	0.4									
Mg	387									
Ca	400									
Na	6	½	5½							
K	0									
Ti	5				5					
O	2667									

Specific Gravity: 3.324

$Ca_{44.9}$ $Mg_{43.5}$ $Fe_{11.6}$

% Al in Z = 4.5

Indices of Refraction
nX 1.6860
nY 1.6906
nZ 1.7137

Pleochroism:
Nonpleochroic
Colorless

Birefringence, x10^4 aver.: 277

256, 275, 286, 290

2V aver.: 48°

45½°, 46°, 46°, 46 3/4°, 47°, 47½°, 48 3/4°, 49¼°, 48 3/4°, 51¼°, 52½°

Z∧c aver.: 42¼°

40 3/4°, 41¼°, 41 3/4°, 41 3/4°, 42½°, 42 3/4°, 44 3/4°

Sample purity: 99.8%

the pattern of 35-9N. Several other unidentified reflections occurred at random in two patterns (35-6N, 35-32N), most of them occurring in 35-6N, the specimen with the lowest purity. While unidentified reflections which occur randomly are due to sample impurity, it is doubtful that this explanation will serve for unidentified lines which persist from specimen to specimen. Line 1, and possibly line 3 of Table 15 fall into this category, hence another explanation must be sought for them.

Modern theories (Fyfe, 1951) propound that bond type as well as ionic radius governs the isomorphous substitution of atoms. In ionic crystals no restrictions are imposed on the bonds; therefore atoms having similar ionic radii will be able to replace one another, and the resulting coordination can be predicted by the radius ratio rule. In covalent crystals the radius ratio rule does not hold. Here the directional properties of the bonds determine the polyhedral configuration, the acceptance or rejection of possible replacements, and therefore the extent of isomorphous substitution. To complicate the situation is the well-known fact that most bonds are a combination of the two types mentioned above. The partial covalence of ionic bonds shortens the ionic radius sum, thus resulting in a distorted configuration which partially controls the acceptance of atoms available for substitution. The type of bonding between any cation and anion is a function of their electronegativities, and the amount of ionic character of the resulting bond can be predicted from the difference in electronegativity between the two (Pauling, 1939).

Table 15. Unidentified Lines: *d*-Spacings and Intensities

Line	35-1N		35-5N		35-6N		35-8N		35-9N	
	d	I/I_0	*d*	I/I_0	*d*	I/I_0	*d*	I/I_0	*d*	I/I_0
1	3.115	5	3.099	5	3.118	5	3.097	5		
2					1.922	5				
3					1.691	5				
4					1.359	5				

Line	35-13N		35-19N		35-24N		35-25N		35-32N	
	d	I/I_0	*d*	I/I_0	*d*	I/I_0	*d*	I/I_0	*d*	I/I_0
1	3.124	10	3.087	5	3.097	10	3.140	10	3.005	5
2										
3										
4									1.692	5

In order to obtain a clear picture of clinopyroxene structure, therefore, it is advisable to consider the following mutually related factors (Table 16): ionic radii, radius sum, radius ratio, coordination number, electronegativity, and per cent covalency. Whereas in diopside the total effect of these factors on the structure is constant, a complex situation arises in the case of other clinopyroxenes where variability of total effect, and hence structure, might be suspected because of the extreme variability of clinopyroxene composition. It should be noted at this point that no major deviation between clinopyroxene and diopside structures is possible, since the fundamental motif, the manner is which the silica tetrahedra are joined, is the same in both cases. The unidentified lines of Table 15 which persist from specimen to specimen indicate that substructural changes do take place, however, and it will be the purpose of what follows to suggest possible reasons for their occurrence.

Table 16. Factors Affecting Structure of Clinopyroxenes

	Cation	Ionic Radius	Anion	Radius Sum	Radius Ratio	C.N.	Elec-neg.	% Coval.*
W—	Ca^{+2}	.99	O^{-2}	2.39	.707	8	2.5	24
	Na^{+1}	.95	O^{-2}	2.35	.679	8	2.6	21
	K^{+1}	1.33	O^{-2}	2.73	.950	9	2.7	19
X—	Mg^{+2}	.65	O^{-2}	2.05	.464	6	2.3	28
	Fe^{+2}	.75	O^{-2}	2.15	.536	6	1.85	43
	Mn^{+2}	.80	O^{-2}	2.20	.571	6	2.1	35
	Ni^{+2}	.69	O^{-2}	2.09	.493	6	1.8	44
Y—	Al^{+3}	.50	O^{-2}	1.90	.357	4	2.0	37
	Fe^{+3}	.60	O^{-2}	2.00	.429	6	1.7	49
	Cr^{+3}	.64	O^{-2}	2.04	.457	6	1.9	41
	Ti^{+4}	.68	O^{-2}	2.03	.486	6	1.9	40
Z—	Si^{+4}	.41	O^{-2}	1.82	.293	4	1.7	49
	Al^{+3}	.50	O^{-2}	1.90	.357	4	2.0	37

* The per cent covalency values were obtained from the electronegativities by reference to Pauling's curve (1939).

A solution to part of the problem lies in the realization that polyhedral configurations found in the diopside structure cannot help being modified in more chemically complex clinopyroxenes. Such a modification is suggested by the absence of several diopside reflections in some of the clinopyroxene diffraction patterns. In the diopside structure Ca has a coordination number of 8, Mg of 6, with respect to surrounding oxygens.

In more complex clinopyroxenes, Ca is replaced by W (Ca^{+2}, Na^{+1}, K^{+1}) and Mg by X, Y (Mg^{+2}, Fe^{+2}, Mn^{+2}, Ni^{+2}; Al^{+3}, Fe^{+3}, Cr^{+3}, Ti^{+4}.) If the crystal is regarded as strictly ionic, some modification of polyhedral distances will result from discrepancies in ionic radii, and in two instances (K in W, Al in Y) a change in coordination can be predicted. This situation is further complicated by the fact that clinopyroxene is not strictly ionic, hence M-O (cation-oxygen) bonds resulting from various substitutions exhibit a range of type, some being more covalent than others. Partial covalence has the effect of shortening inter-atomic distances, imposing directional restrictions, and in some cases producing resonance. All three of these may lead to configuration and/or coordination changes. Furthermore, the introduction of one element into a given position affects the electronegativity of surrounding oxygens, and hence influences the acceptance or rejection of possible neighboring atoms.

Of particular interest is the effect which substitution of Al for Si in the silica tetrahedra has on further substitutions. Al is more electropositive than Si; therefore when it replaces Si the bonds to the neighboring oxygen atoms become more ionic, and as a result the O-M bonds (bonds from non-bridging oxygens to metal ions) become more covalent. It should be expected, therefore, that these more covalent sites (i.e., more covalent than around Si-O bridges) will be attractive to covalent atoms on the verge of substitution. This is verified by the proportional increase of Fe^{+2}/Mg ratio in silicates as more and more Al substitutes for Si (Ramberg, 1952). This neat relationship obtains only when all other factors are constant; i.e., when only Fe^{+2} and Mg have to be considered. Since Fig. 4 fails to show such a simple relationship, it is evident that other substituting elements must be influential in the case of chemically complex clinopyroxenes.

It is a well-known fact (Ramberg, 1952) that the amount of Al in Si positions increases as polymerization of silicate structure is developed to a higher degree (tectosilicates have more Al in Si positions than do nesosilicates). But this does not explain why different amounts of Al enter Si sites in clinopyroxenes where the degree of polymerization is supposedly constant. Nor does it explain increase of Al substitution for Si concomitant with increase of total Al present (Fig. 5). Since such a relationship between total Al and per cent Al in Z does exist, it is tempting to suggest that geochemical conditions which supplied Al were also influential in determining degree of acceptance of Al in Si positions, and that the introduction of Al into Si sites causes partial polymerization of chains giving rise to clinopyroxenes that are transitional between single and double chain inosilicates. Such a condition might arise in the following way. If for the moment the crystal is regarded as ionic, there will be,

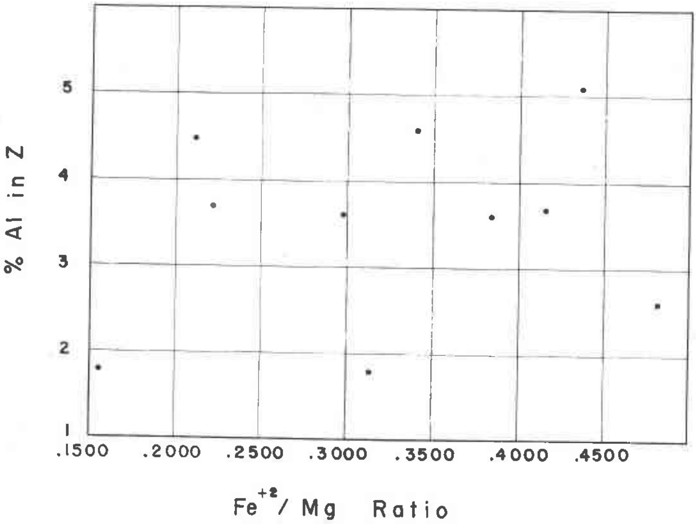


FIG. 4. Relation between % Al in Z and Fe^{+2}/Mg ratio.

as noted before, a drop in coordination number from 6 to 4 when Al substitutes for Si. This means that there are two oxygens "left over." It is not hard to visualize a situation in which these oxygens become shared by tetrahedra in adjacent chains. Such partial polymerizations

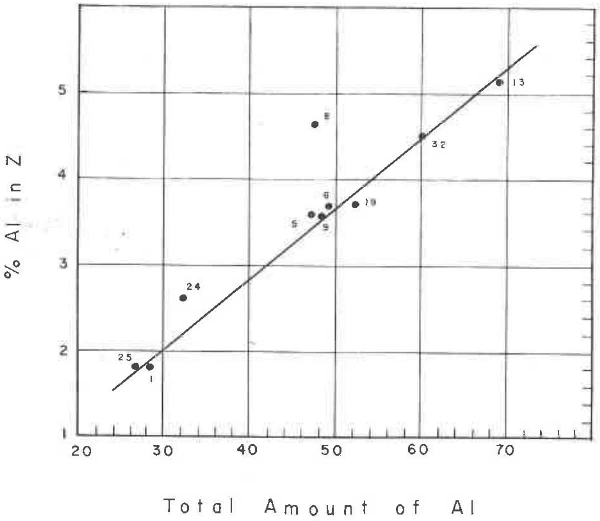


FIG. 5. Relation between % Al in Z and total amount of Al (atomic ratio).

are substructural changes, and when they are developed to a certain degree it is reasonable to expect that they will be detected by *x*-ray diffraction procedures. When they are developed beyond a certain limit the *x*-ray beam, which records statistically, will note a structural change, i.e., the change from single to double chains.

The geochemical conditions held responsible above both for supplying Al and controlling its substitution for Si remain unknown. But one clue, the known transition of pyroxene to amphibole in metamorphic rocks, such as phyllite and schist, which have been subjected to direct componental stresses enables us to speculate that conditions other than those prevalent in igneous reaction series, namely the presence of directed stresses, foster the entrance of Al into Si sites causing the partial polymerization of silicate chains.

On the basis of the several lines of evidence presented in this section, (*a*) the presence of strong persistent unidentified reflections on diffraction curves, (*b*) the absence of several diopside reflections in clinopyroxene diffraction patterns, (*c*) theoretical considerations which enable us to visualize numerable adjustments of polyhedral distances, configurations, and coordinations, and (*d*) widely variable and probably highly influential geologic conditions, it is postulated that substructural changes occur in chemically and/or geologically complex clinopyroxenes. It will be the purpose of another paper to study these changes in detail.

OPTICAL CRYSTALLOGRAPHY

It would be difficult to add anything to the excellent optical property curves for clinopyroxenes given by Hess (1949). In constructing these curves it was assumed that the following amounts of minor oxides were present:

	%
Al_2O_3	3.0
Fe_2O_3	1.5
Na_2O	0.4
TiO_2	0.4
MnO	0.3
Cr_2O_3	1.1

Since the actual amounts of minor oxides present in the clinopyroxenes of this study differ from the values given above, some of the optical properties observed (Tables 5–14) differ from those predicted from chemical composition (expressed in terms of Ca:Mg:Fe ratios, Fig. 6) using the optical property curves of Hess. Optical properties which show the greatest deviation from predicted values are 2V and birefringence. In both these cases deviations from predicted values seem to be

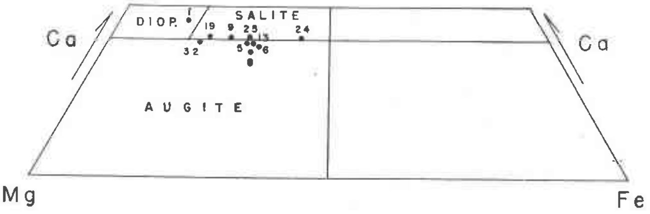


FIG. 6. Partial ternary diagram showing compositions of clinopyroxenes in terms of Ca:Mg:Fe ratios. Ni is added to Mg; Fe^{+3} and Mn are added to Fe^{+2}.

especially related to differences between the assumed amount of Al_2O_3 and the amount actually present in the particular clinopyroxene being studied. Figures 7 and 8 show these relationships. Agreement between the three indices of refraction and their predicted values is good, the maximum discrepancy being ±.007, the average ±.003.

Another type of discrepancy should be mentioned here, namely, the discordance or range of values obtained in the measurement of optical properties both in this and in other studies. While cumulative errors cause some of the discordance, the wide ranges observed in many cases

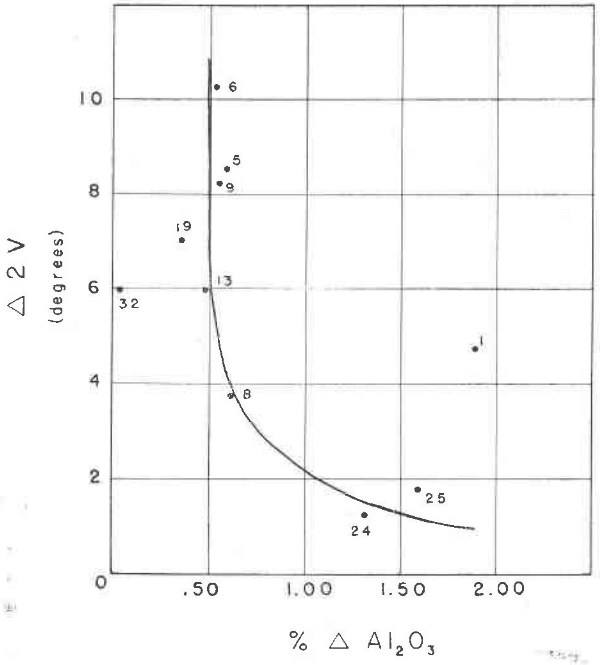


FIG. 7. Relation between 2V and % Al_2O_3.

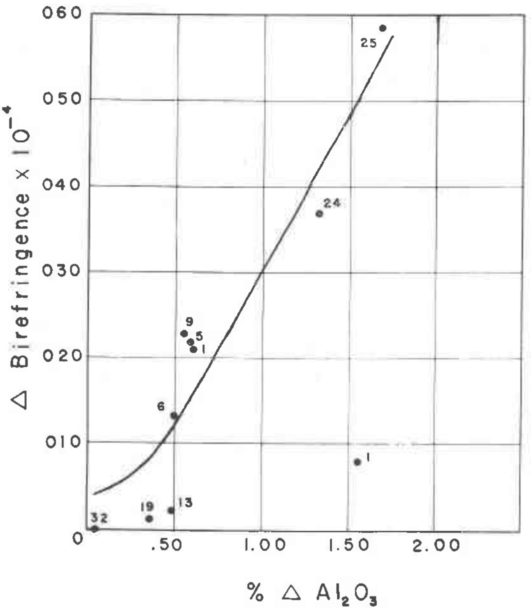


FIG. 8. Relation between birefringence and % Al_2O_3.

demand a more suitable explanation. Perhaps the answer lies in the fact that there is no reason why all grains of a chemically complex mineral should be exactly the same. If the complex history of most rock bodies, and particularly metamorphic ones, is called to mind, situations can indeed be visualized which would vary both the elemental supply and the physical-chemical conditions at various portions of the rock body. Hence inter-grain variation could be due to either different elemental supply or different physical-chemical conditions. Furthermore, wide intra-grain variation should be expected in chemically complex minerals such as clinopyroxene where random distribution of metal cations produces lattice planes in which all directions are singular. Since average optical parameters are generally arrived at from measurements taken from several grains, both these features of complex minerals in complex rocks, inter-grain and intra-grain variation, would lead to the discordance obtained in the measurement of optical properties.

GEOCHEMISTRY

Detailed structural and petrologic studies of the Wilmington gabbroic complex (Ward, 1958) show beyond doubt the metamorphic character of the rocks containing the clinopyroxenes. Although the clinopyroxenes

TABLE 17. Fe^{+2}/Mg RATIOS OF CLINOPYROXENES

Sample	Hypersthene	Clinopyroxene	Δ Fe^{+2}/Mg
35-1	*	.1552	
35-5	.7021	.3846	.3175
35-6	.7413	.4164	.3249
35-8	.6344	.3415	.2929
35-9	.5767	.2988	.2719
35-13	.7755	.4373	.3382
35-19	.4151	.2228	.1923
35-24	†	.4821	
35-25	†	.3141	
35-32	.3712	.2119	.1593

* Hy present but not studied.
† No Hy present.

have had a metamorphic evolution, several lines of geochemical evidence exist which indicate that they were originally of igneous genesis. When dealing with the crystallization of igneous rocks it is to be expected that as the series olivine→orthopyroxene→monoclinic pyroxene→hornblende progresses, both Fe^{+2}/Mg and Mg/Ca ratios will simultaneously decrease (Rankama, 1950). Tables 17 and 18 give the Fe^{+2}/Mg and Mg/Ca ratios of the clinopyroxenes of this paper and their coexisting hypersthenes studied by Clavan (1954). The igneous origin of these coexisting pairs is shown by the fact that both the Fe^{+2}/Mg and Mg/Ca ratios of hypersthene are greater than those of clinopyroxene.

Since igneous orthopyroxenes are more ferrous than their monoclinic

TABLE 18. MG/CA RATIOS OF CLINOPYROXENES

Sample	Hypersthene	Clinopyroxene	Mg/Ca
35-1	*	.9094	
35-5	3.9000	.8376	3.0624
35-6	3.0437	.8271	2.2166
35-8	2.8722	.8711	2.0011
35-9	3.8643	.8711	2.9932
35-13	1.3235	.8267	0.4968
35-19	3.1200	.9292	2.1908
35-24	†	.6802	
35-25	†	.8146	
35-32	1.6436	.9675	0.6761

* Hy present but not studied.
† No Hy present.

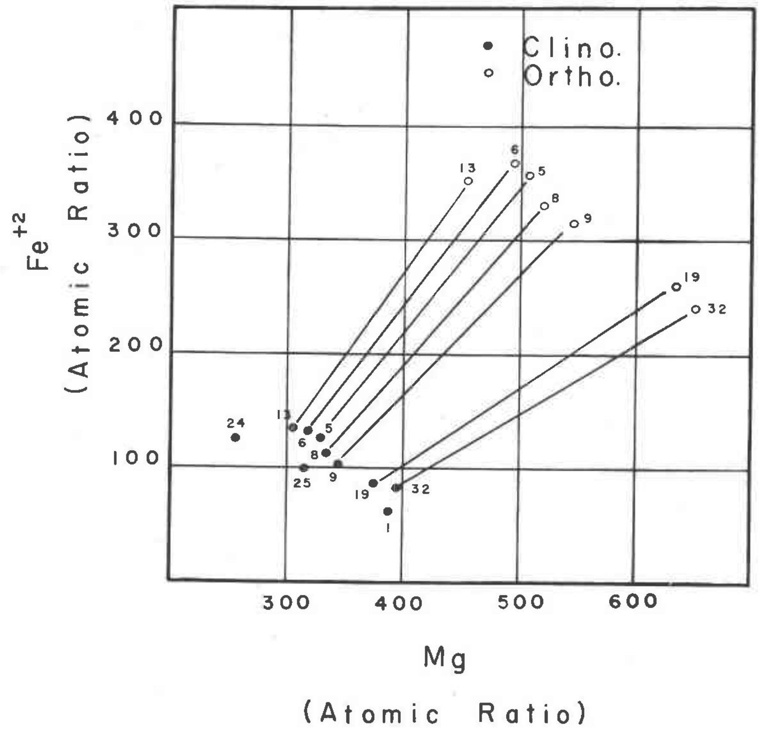


FIG. 9. Clinopyroxene-orthopyroxene partition based on molecular ratios of Fe^{+2} and Mg.

counterparts, further evidence supporting the igneous origin of the pyroxenes studied here is given by Fig. 9. This shows there is a definite partition between hypersthene and its coexisting clinopyroxene, hypersthene being more ferrous and more magnesian than clinopyroxene.

In his paper on the "Pyroxenes of Common Mafic Magmas" Hess (1941) showed that if the compositions of coexisting igneous pyroxenes are plotted on an En:Fs:Wo ternary diagram, the clinopyroxene-orthopyroxene joins converge to $En_{25}Wo_{75}$, and composition of one pyroxene can be predicted if the composition of its counterpart is known. Figure 10 shows the general convergence of clinopyroxene-orthopyroxene joins to $En_{25}Wo_{75}$ for the pyroxenes studied here. This convergence is further indication of their igneous origin. Lack of absolute convergence to $En_{25}Wo_{75}$ is a reflection of the masking effects of metamorphic processes.

Whereas the three lines of evidence mentioned above (*a*) the decrease in Fe^{+2}/Mg and Mg/Ca ratios going from orthopyroxene to clinopyrox-

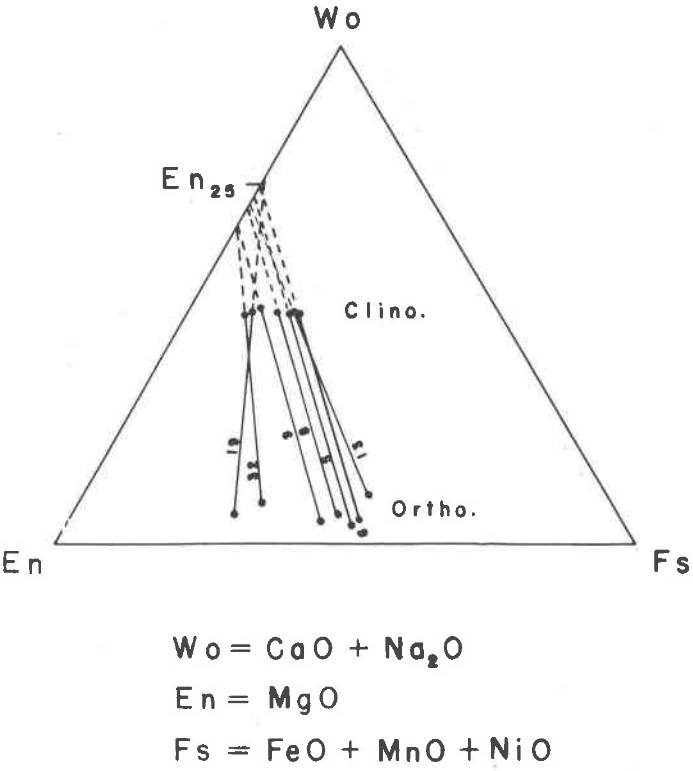


FIG. 10. Convergence of clinopyroxene-orthopyroxene joins.

ene, (*b*) the predominance of ferrous iron in orthopyroxenes rather than in clinopyroxenes, and (*c*) the convergence of clinopyroxene-orthopyroxene pairs to $En_{25}Wo_{75}$, indicate that the rocks studied here are of igneous origin, lack of correspondence between certain expected and observed geochemical relations offers some insight to their complex evolution.

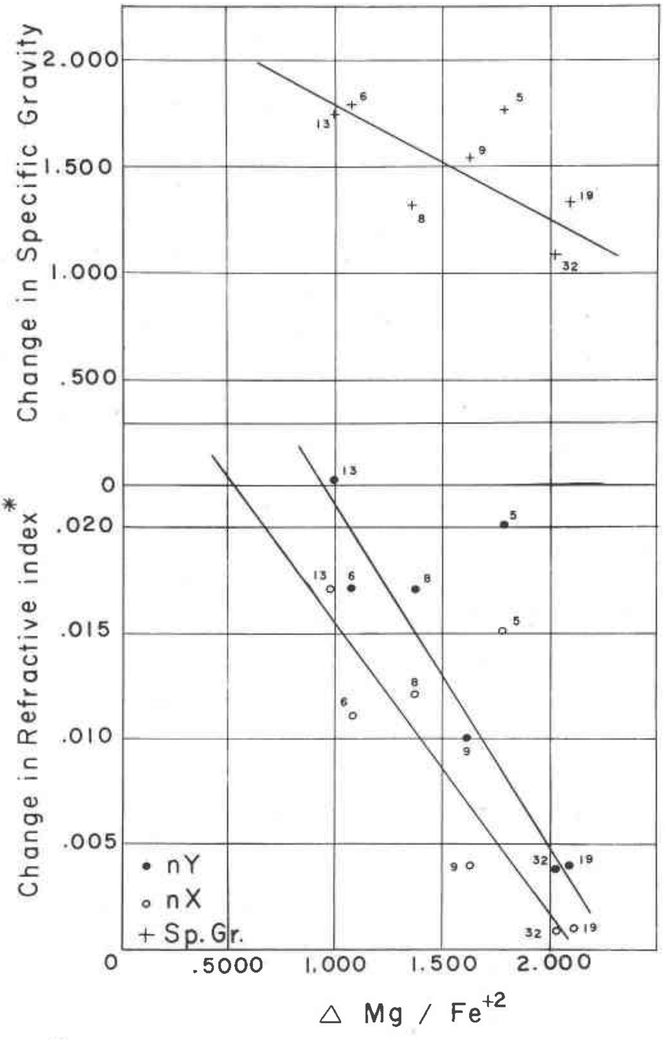
In the normal igneous situation orthopyroxene will be less magnesian than clinopyroxene. From the partition shown in Fig. 9 it is seen that for the pyroxenes studied here the opposite relation holds. This suggests that Mg has been introduced during metamorphism and for some reason has been concentrated in orthopyroxenes rather than clinopyroxenes.

In a truly igneous rock there is no equilibrium between pyroxene counterparts since they are members of one reaction series. According to Ramberg (1952) if equilibrium does exist between orthopyroxene and clinopyroxene in the same rock, the Mg/Fe^{+2} ratio will increase in going from orthopyroxene to clinopyroxene. Such an increase is shown between pyroxene pairs from rocks of the Piedmont Province indicating that equilibrium has been established, but further evidence must be obtained before accepting this idea.

If equilibrium has been established between pyroxene pairs, it is possible that it was brought about by the introduction of Mg during metamorphism. Figure 11 shows that the change in indices of refraction and specific gravity between ortho- and clinopyroxene is related to the change in Mg/Fe^{+2} ratio suggesting that the optical properties of one or both pyroxenes have been modified by their metamorphic evolution.

Summary of Experimental Observations

1. Specific gravities of clinopyroxenes increase proportionally as mole per cent ferrous silicate increases.
2. Good results are obtained by both the cleavage and zone methods of measuring extinction angles.
3. Diffraction patterns of clinopyroxenes contain persistent unidentified reflections which are believed to be due to substructural differences between complex clinopyroxenes and diopside.
4. A number of diopside lines are omitted on clinopyroxene diffraction patterns.
5. No relationship exists between Fe^{+2}/Mg ratio and amount of Al in Si sites for clinopyroxenes studied here.
6. The per cent of Al in Z is proportional to the total amount of Al present.
7. The difference between optical properties determined in this paper and values predicted from chemical composition using the curves of Hess (1949) are accounted for by the difference between actual and assumed amounts of minor oxides.
8. Differences between the assumed and actual amount of Al_2O_3 particularly seem to explain deviations of 2V and birefringence from predicted values.
9. Good agreement is obtained between the three indices of refraction and their predicted values.
10. Wide ranges were obtained in the measurement of some optical properties.
11. Fe^{+2}/Mg ratios of hypersthenes studied by Clavan (1954) are greater than those of coexisting clinopyroxenes.
12. Hypersthenes (Clavan, 1954) are richer in both Mg and Fe^{+2} than their clinopyroxene counterparts.
13. Clinopyroxene-orthopyroxene joins show a general convergence to $En_{25}Wo_{75}$ on an En:Fs:Wo ternary diagram.



* Changes in nZ did not exhibit a wide enough range to be plotted.

FIG. 11. Relation between change in refractive index and specific gravity and change in Mg/Fe^{+2} ratio.

14. The Mg/Fe^{+2} ratio increases in going from orthopyroxene to clinopyroxene.
15. Changes in indices of refraction and specific gravity between orthopyroxene-clinopyroxene pairs are related to change in their Mg/Fe^{+2} ratio.

CONCLUSIONS

The clinopyroxenes studied here are of igneous origin but have undergone subsequent metamorphism. During metamorphism Mg may have been introduced and concentrated in the coexisting orthopyroxene rather than in clinopyroxene. This possibly has produced equilibrium between clinopyroxene and orthopyroxene existing in the same rock. The optical properties of one or both pyroxenes have been modified by their metamorphic evolution. This also produced inter-grain and intra-grain variations which explain the wide ranges obtained in the measurement of some of the optical properties. Physical geologic conditions are also probably influential in determining (*a*) the amount of Al entering Si tetrahedra and (*b*) polyhedral distances, configurations, and coordinations. Considering this and the possible substitutions in clinopyroxenes leads to a picture of variable polyhedral distances, configurations, and coordinations in chemically and/or geologically complex clinopyroxenes, and to the suggestion that they may be substructurally different from diopside. Substructural difference is also suggested by the presence of persistent unidentified lines and by the omission of diopside lines in *x*-ray diffraction patterns of clinopyroxenes.

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