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# X-RAY DIFFRACTION MEASUREMENTS UPON THE PYROXENES.

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### INTRODUCTION.

Detailed chemical and optical studies have been made by two of the present writers¹ upon a number of pyroxene minerals. The present X-ray measurements were undertaken partly to throw light on certain specific problems suggested by the previous work and partly to discover how much useful information can be obtained from an examination of less simple mineral groups by employing the existing X-ray diffraction methods.

In the course of this work powder photographs have been made of examples of the different types of minerals that have from time to time been grouped amongst the pyroxenes. These photographs have served to divide the minerals studied into groups with related X-ray patterns and hence with the same types of crystal structure. Where several minerals with different chemical compositions but the same sort of pattern were available, the photographs were analyzed to determine the effects of atomic replacements in changing the absolute size of the structure.

Partial accounts of these experiments are contained in papers read at the December, 1923 and the December, 1924 Meetings of the Mineralogical Society of America. A brief summary of some of the results has also been published.<sup>2</sup>

Many of the specimens used in this study were obtained from the United States National Museum through the kindness of W. F. Foshag. We are also indebted to E. V. Shannon for a sample of bustamite and to E. S. Shepherd not only

<sup>&</sup>lt;sup>1</sup>H. S. Washington and H. E. Merwin, Am. Min. 7, 121, 1922; ibid. 8, 63, 114, 215, 1923; this Journal, 3, 117, 1922; etc.

<sup>2</sup> R. W. G. Wyckoff, The Structure of Crystals, p. 417, New York, 1924.

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for supplying us with some hedenbergite from Herault, California, but for allowing us to give here his hitherto unpublished analysis of this material.

## METHODS AND RESULTS.

Powder photographs were made in the usual way,<sup>3</sup> the sample having the form of a thin film with collodion as a binder. The spectrograph was standardized by averaging the crystal-to-film distances calculated from several photographs of sodium chloride powder. This procedure is not so accurate as one in which sodium chloride, or other standard crystal, is

TABLE I. The Spacings of Conspicuous Powder Lines of Diopside and of Kilimanjaro Augite, and their Ratios.

Spa	ncing	
Diopside	Kilimanjaro Augite	Ratio
0.914A°	0.913A°	0.999
1.070	1.064	.994
1.144	1.145	1.001
1.283	1.274	.993
1.325	1.318	.995
1.414	1.405	.994
1.499	1.500	1.001
1.617	1.618	1.001
1.745	1.737	.995
1.827	$1.823_{5}$	.998
2.023	2.011	•994
2.133	2.118	.993
2.207		
2.527	2.535	1.003
2.979	2.984	1.002

o.997 = Average Spacing Ratio for Kilimanjaro Augite

mixed directly with the powder under examination. The pyroxenes, in common with a majority of low-symmetry crystals, give X-ray patterns which are relatively weak, and yet rich in lines. For this reason and because of certain more

<sup>&</sup>lt;sup>3</sup> R. W. G. Wyckoff, loc. cit., Chap. VI.

### TABLE II. The Powder Patterns of the Pyroxenes.

Mineral

Type Chemical Formula

Diopside-like Pattern

Diopside Hedenbergite Acmite

 $CaMg(SiO_3)_2$  $CaFe''(SiO_3)_2$ NaFe'''(SiO\_3)\_2  $NaAl(SiO_3)_2$ 

**Tadeite** Augite

Ca(Mg, Fe) (SiO<sub>3</sub>)<sub>2</sub>.x(Fe'", Al),O<sub>2</sub>

#### II. Enstatite-like Pattern

Enstatite Hypersthene MgSiO<sub>3</sub> (Mg, Fe)SiO<sub>3</sub>

### III. Wollastonite-like Pattern

Wollastonite Bustamite Pectolite Schizolite

CaSiO<sub>3</sub> (Ca, Mn)SiO<sub>3</sub>  $(Na,H)_2Ca_2(SiO_3)_3$  $(Na, H)_{\mathfrak{g}}(Ca, Mn)_{\mathfrak{g}}(SiO_{\mathfrak{g}})_{\mathfrak{g}}$ 

### IV. Rhodonite-like Pattern

Rhodonite Ca-rich rhodonite MnSiO<sub>3</sub> (Mn, Ca)SiO<sub>3</sub>

## V. Other Types of Pattern

The following minerals, frequently classified as pyroxenes, give patterns which apparently are unlike one another or any of the preceding four.

Clino-enstatite Spodumene

 $MgSiO_3$ LiAlSiO,  $PbSiO_3$ 

Alamosite Pyroxmangite

 $x(Ca, Fe'', Mn)O.y(Fe''O, Al_2O_3).$ 

Sobralite<sup>1</sup>

 $(SiO_2)_{(x+4y)}$   $(Mn_4, Fe_2'', Ca, Mg)_{(SiO_3)_8}$ 

The pattern of babingtonite—x(Ca, Mg, Fe",H2)O.y[(Na2,-Fe'')O(AlFe''')<sub>2</sub>O<sub>3</sub>].(SiO<sub>2</sub>) (x+4y) —probably is different from that of wollastonite, it certainly is unlike that of any other pyroxene.

<sup>&</sup>lt;sup>1</sup>Bull. Geol. Inst. Univ. Upsala 14, 109, 1917.

or less necessary approximations in the subsequent treatment of the data, more accurate measurements were not deemed of real value for the present purposes. The results recorded in this paper have a probable error of from 0.3 to 0.4 per cent.

Diopside and other minerals structurally isomorphous with it give better powder photographs than any of the other pyroxenes. The unit cell of diopside, and its space group, have already been determined from a study of Laue and spectrum photographs produced by a single crystal.<sup>4</sup> From this knowledge the positions of all of the powder reflections of diopside can be calculated and it should thus be possible to assign indices to the various observed powder lines. When this procedure is carried out, however, it is found that conceivable reflections lie so close together that unique index assignments can rarely be made for the observed lines. If the structure of diopside were completely known, the intensity distribution between these lines could be calculated, but until this is possible or until a much greater resolution can be obtained in powder photographs than is now practicable, index assignments in such powder photographs as these will have little physical significance.

Since it is not feasible to measure directly the sizes of the unit cells of the various crystals under investigation, resort must be had to an indirect mode of comparison. present experiments this comparison was furnished by taking the lines of one mineral of each structure type as standard and calculating the ratio of the spacings of the corresponding lines from each of the others. The average of these relative spacings for a single mineral is its average spacing ratio. For the diopside-like minerals, diopside itself has been used as the standard; this method of calculation will be clear from the spacing data of the structurally isomorphous augite from Kilimanjaro reproduced in Table I. Such a process is not an ideal one but if enough lines are available and if, as is true for most of the pyroxenes studied here, marked differences do not exist in the axial ratios, then the averages obtained in this way will be an approximate measure of the relative sizes of their unit cells.

X-ray examination shows that with a few exceptions all the available minerals that have been classed with the pyroxenes give patterns of one of four different types. Tracings of powder photographs of each of these sorts, of which diopside,

<sup>&</sup>lt;sup>4</sup>R. W. G. Wyckoff and H. E. Merwin, this Journal, 9, 379, 1925.

enstatite, wollastonite and rhodonite are typical, are shown in

Figure 1.

Their powder photographs show that the minerals grouped together in Table II have similar patterns and therefore closely related structures. In the subsequent discussion of the measurements on these minerals it will be convenient to treat together those substances which give similar patterns.

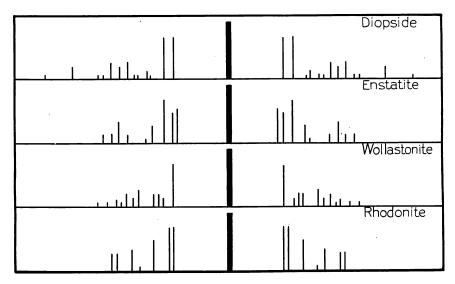


Fig. 1.—Tracings of powder photographs of diopside, enstatite, wollastonite and rhodonite. In this figure actual positions of lines on the film are plotted as abscissas, relative intensities as ordinates.

## DIOPSIDE GROUP.

The diopside-like pyroxenes are more numerous and in general give better photographs than those of any other group. The particular minerals subjected to X-ray examination are listed in Table III; analyses of several of them are recorded in Table IV. Their relative spacings as measured from the powder photographs and calculated in the manner outlined in Table I are given in Table V. To facilitate comparison between these results, the relative spacings are repeated in Table VI together with the analyses calculated in terms of the atomic composition of a theoretical diopside. Following this

TABLE III. Diopside-like Minerals Examined by X-rays.

Diopside. Locality: Ham Island, Alaska. Analysis: Table This material was the standard of comparison for all mem-

bers of this isomorphous group.

- Acmite. An artificial preparation. Very pure.
- An unanalyzed sample from Middle America. Tadeite. 3.
- Hedenbergite Herault —. Locality: Herault, California. Analysis: Table IV.
  - Japanese —. Locality: Kamioka, Japan. U. S. N. M. No. 61877.

Augites

Haleakala —. Locality: Haleakala, Maui, Hawaiian 5a. Islands. Analysis: Table IV.

Kilimanjaro —. Locality: Kilimanjaro, Africa. Analysis: Table IV.

Villa Senni —. Locality: Villa Senni, Alban Hills, 5c. Italy. Analysis: Table IV.

Fosso Tavolato —. Locality: Alban Hills, Italy. Analysis: Table IV.

Nordmark —. Locality: Nordmark, Sweden. U. S. National Museum No. 79170. Analysis: Table IV.

"Green Rhodonite." Locality: Broken Hill, New South 5f. Wales.

Analysis: Table IV. "Indian" —. Locality: Bombay, India. Separated from one of the basalts. Analysis: Table IV.

Schefferite. Locality: Langban, Sweden. U. S. National Museum No. 47455. Specimen not analyzed.

method of expression the number (usually a fraction) of atoms combined in each molecule of  $(R_1, R_2, \ldots)$  (R', R'',.....) (Si, Ti)<sub>2</sub>O<sub>6</sub> are stated. Atoms  $R_1$ ,  $R_2$ , ... etc. are considered to be magnesium, calcium and those divalent atoms replacing them; R', etc. are sodium and ferric iron and any others replacing them, and the sum of silicon and titanium is always taken as two. In the augite Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> are expressed as the number of these molecules to every pair of

Table IV. Chemical Analyses of Several of the Diopside-like Pyroxenes Examined by X-rays.

Composition	Villa Senni	Kilima	njaro	Haleal	kala	Fosso	Tavolato
$SiO_2$	46.16	48.	16	47.7	o		48.11
${ m TiO_2}$	2.86	0.	59	1.8	9		1.19
$Al_2O_3$	4.92	8.	45	6.8	2		5.45
$\mathrm{Fe_2O_3}$	5.89	2.	86	3.3	6		4.42
FeO	3.93	3⋅	55	4.4	3		3.74
$_{ m MgO}$	11.29	14.	23	13.3	4		12.03
CaO	23.56	21.	69	21.3	5	:	24.50
$\mathrm{Na_2O}$	0.42	0.	91	0.6	5		0.46
$K_2O$	0.11	0.	10	0.0	3		none
$\rm H_2O+$	• • • •			O.I	5		0.09
MnO	• • • •	0.	10	0.1	6		0.09
Analyst:	Washington	Washin	gton	Washir	ngton	Wa	shington
Reference:	Unpublished			Am. J.			ı. Min. 8,
Remarks:	Incomplete	121 (1	922)	3, 117 (	19 <b>2</b> 2)		(1923)
Kemarks.	Incomplete 1913					1.54	2% Cr <sub>2</sub> O <sub>3</sub>
	-9-3						
					"Gr	een	Ham Island
omposition	Indian	Herault	Nord	lmark	Rhodo		Diopside
S:O	FO 20	18 21	<b>~</b> ~	) T 4	40	20	- 46-

Composition	Indian	Herault	Nordmark	"Green Rhodonite"	Ham Island Diopside
Composition	man		Norumark		•
$\mathrm{SiO}_2$	50.39	48.34	52.14	48.30	54.65
${ m TiO_2}$	0.44	0.08			
$\mathrm{Al_2O_3}$	3.27	0.30	1.81	3.22	
$\mathrm{Fe_2O_3}$	1.50	1.50	0.49	2.04	0.13
FeO	21.27	22.94	13.47	17.10	
$_{ m MgO}$	11.80	1.06	9.35	none	18.78
CaO	10.89	21.30	23.25	22.55	25.27
$\mathrm{Na_{2}O}$	0.28	0.14		• • • •	0.03
$K_2O$	0.05	0.03			0.07
$\mathrm{H_{2}O}{+}$	0.10	0.46			1.45
MnO	0.41	3.70		7.10	• • • •

Analyst: Washington E. S. Shepherd Washington Searcy Allen Reference: Unpublished Unpublished Unpublished Mem. Geol. Analysis Survey N.S.W. 27, 1, (1909)
Incomplete App. II, 334

(Si + Ti) atoms, i. e. to every molecule of diopside itself. This method of expression has the advantage of showing immediately the relative numbers of the different kinds of atoms and whether either the calcium or magnesium-like atoms are present in excess of the normal one-to-one diopside ratio.

The most striking fact arising from these X-ray measurements is the very close similarity in spacings, and consequently

in size of unit cell, between diopside itself and these minerals with widely different chemical compositions. In all cases except that of jadeite the average spacing difference from diopside is much less than one per cent. Jadeite is found only under conditions which indicate the existence of a high pressure at the time of its formation. The necessary minerals

Table V. The Average Spacing Ratios for Diopside-like Minerals.

	(Diopside	as	Stand	lard)
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		Hedenbergite Augi				
Film No.	Acmite	Jadeite	Herault	Japanese	Haleakal <b>a</b>	
I	.995	.976	1.004	1.004	.998	
2	·995	.971	1.006	1.004	.998	
3	.994	.976	1.003		1.000	
4	.994	.972	1.004	• • • •	.998	
	.9945	.974	1.004	1.004	.9985	

## Augite

Film No.	Kilimanjaro	Villa Senni	Fosso Tavolato	Nordmark
I	•997	1.002	1.000	1.001
2	.997	1.002	000.1	1.002
3	.998			1.001
4	.996		• • • •	.999
	·997	1.002	1.000	1.001

## Augite

Film No.	"Green Rhodonite"	"Indian"	Schefferite
I	1.010	1.000	.999
2	1.002	1.001	1.002
3	1.006	1.000	.998
4	1.010	1.001	.999
	1.007	1.0005	.999₅

were not available to show whether jadeite can hold appreciable quantities of other diopside-like substances in solid solution at ordinary temperatures and pressures. It will be of interest to see whether X-ray spacings from many other and more varied diopside-like minerals will lie within the very restricted limits found for the minerals described in this paper.

TABLE VI. Compositions, Average Spacing Ratios and Densities of Diopside-like Pyroxenes.

Composition Ca	Ham Island Diopside . 0.991	Herault Hedenbergite 0.943	Haleakala Augite 0.931	Kilimanjaro Augite 0.956
Mg		.065	.809	
Fe"	•	.792	.151	.122
Mn		.129	.005	.003
		<del></del>		
Sum of diopside-like bas	es 2.015	1.929	1.896	1.953
Acmite-like bases	. <0.01	.026	.106	.156
•	<del></del>	<del></del> .		
Sum of all bases	. 2.015	1.955	2.002	2.109
Excess $Fe_2O_3$	. <0.01	.017	.025	.003
Excess $Al_2O_3$		.007	.164	.205
Sum of excess $R_2O_3$ .		0.024	0.189	0.208
Average Spacing Ratio		1.004	0.999	0.997
Density (observed)		• • • •	3.35	
" (calc. with $R_2O_3$	.)	• • • •	• • • •	
" ( " without "	)		3.40	• • • •

Composition	Villa Senni Augite	Fosso Tavolato Augite		"Green Rhodonite"	"Indian" Augite
Ca	1.045	1.071	0.995	1.000	0.460
Mg	.696	.731	.534	none	.701
Fe"	.136	.128	.432	.592	.693
Mn	• • • •	.003		.249	.013
Sum of diopside-like bases		1.933	1.921	1.841	1.867
Acmite-like bases		.039			.048
Sum of all bases	1.955	1.972	1.921	1.841	1.915
Excess of $Fe_2O_3$	.072	.050	.007	.032	.022
Excess of $Al_2O_3$	.120	.131	.041	.078	.076
Sum of excess $R_2O_3$	0.192	0.181	0.048	0.110	0.098
Average Spacing Ratio	1.002	1.000	1.001	1.007	1.001
Density (observed)		3.36		• • • •	3.46
" (calc. with $R_2O_3$ )		3.73			
" ( " without " ) .	3.39	3.38			3.53
" ( " as mixture)	• • • •				3.48

Further inspection of Table VI shows that a general accord between hypothesis and observation will result if it is assumed: (1) that atoms of magnesium and of ferrous iron have practically the same effective volumes in this structure; (2) that manganese atoms have a somewhat larger volume than these two atoms, and (3) that calcium atoms have a much larger

volume. On the whole these assumptions agree with previous crystal structure measurements. Calcite has a much larger unit cell than have ferrous, manganese or magnesium carbonates.<sup>5</sup> Furthermore pure dolomite and one in which 30 per cent. of the magnesium atoms are replaced by ferrous iron have unit cells which are practically identical in both size and shape.<sup>6</sup> The sizes of the manganese and ferrous carbonates are, however, more nearly the same than the present measurements would suggest.

There is no apparent connection between the amount of excess  $Al_2O_3$  and  $Fe_2O_3$  and the sizes of the unit cells of these minerals. One line, too hazy to be accurately measurable, has been observed in powder photographs of some of the augites. The present experiments, however, are incapable of showing whether or not this reflection is in any way related to the  $R_2O_3$  content; nor is there any other indication from the diffraction photographs of the existence of the excess  $R_2O_3$ .

Such a result is not surprising, for, unless the ferric oxide and alumina were present in crystals which gave exceptionally strong diffraction lines, their patterns probably could not be seen superimposed on that of diopside. Further, if, as some have supposed, the ferric oxide and alumina are present in the diopside structure itself through some sort of an isomorphous replacement, they are not present in sufficient quantities so that their effect would stand out clearly over and above the effects of the other atomic replacements that exist in these minerals. This is true even though, as the measurements on jadeite show, introduction of aluminum atoms into a diopside (acmite) structure should bring about in it a very pronounced shrinkage. The only satisfactory test of such a replacement hypothesis for the excess R<sub>2</sub>O<sub>3</sub> would be obtained by photographing two augites which had practically identical ratios of Ca to Mg and were unlike only in having widely different Al<sub>2</sub>O<sub>3</sub> Such augites were not available for these expericontents. ments.

Even though the present results are unable to show the state of the excess  $R_2O_3$  in augites, they clearly indicate that it cannot exist in the crystal structure of diopside unless it were assumed to replace atoms of this structure. These augites are sufficiently alike crystallographically so that for the present

<sup>&</sup>lt;sup>5</sup> W. L. Bragg, Proc. Roy. Soc., **89**, 468, 1914; R. W. G. Wyckoff, this Journal, **50**, 317, 1920; G. R. Levi and A. Ferrari, Rend. Accad. Lincei, **33**, 816, 1924.

<sup>6</sup> R. W. G. Wyckoff and H. E. Merwin, this Journal, **8**, 447, 1924.

purposes their volumes may be considered as proportional to the cube of their average spacing ratios. Their densities may thus be calculated from the molecular weights given by chemical analyses. In Table VI densities calculated in this way are compared with observations upon several augites. From these data it is apparent that the assumption of the presence in the molecule of the excess R<sub>2</sub>O<sub>3</sub> in addition to the diopside-like metasilicate molecule R' R" (SiO<sub>3</sub>)<sub>2</sub> leads, for the Fosso Tavolate augite, to an impossibly high density ( $\rho = 3.73$  as compared with the observed  $\rho = 3.36$ ). At the same time it is apparent that a complete neglect of the R<sub>2</sub>O<sub>3</sub> gives densities which are in close agreement with observation in all cases where this physical property has been determined. When the comparatively small proportion of the R<sub>2</sub>O<sub>3</sub> is borne in mind, approximate agreement is to be expected either if the oxides are in some kind of isomorphous replacement or if they are in some intimate mechanical admixture in forms having densities that do not vary widely from that of the diopside-like The assumptions underlying these hypotheses of replacement and of admixture cannot be stated with enough precision nor can the limits of proportionality between volume and cube of spacings be known with sufficient accuracy to permit a more detailed use of such calculations of density.

The augite which has been called "Indian" is strikingly different from the others in its content of calcium. Its predominant pattern is diopside-like. Other lines are present, however, which could be the principal ones of an enstatite-like structure. It thus is compatible with the observed measurements, though these measurements do not furnish final proof, that this "Indian" augite is an intimate mixture of materials having these two structures. The density of such a mixture can be calculated on the assumption that the diopside constituent is normal with respect to calcium and that the (Fe + Mg) in excess of the amount necessary to combine with it is present as a hypersthene. The density calculated on this basis is close to the observed density (see Table VI).

## ENSTATITE GROUP.

Powder photographs have been prepared and analyzed from three minerals giving the pattern of enstatite. They are listed in Table VII. Chemical analyses of two of them are reproduced in Table VIII.

In the experiments previously reported no difference could

be observed between the patterns of typical natural enstatite and typically twinned clino-enstatite, produced by quickly cooling a MgSiO<sub>3</sub> melt. Their apparent identity suggested that enstatite might be submicroscopically twinned clino-enstatite. The optical properties as far as known can be made to fit this

TABLE VII. Enstatite-like Minerals Examined by X-rays.

I. Enstatite. Locality: Espedalen, Norway.

Analysis: Table VIII.

An average from six films of this material was the standard of comparison for other members of this isomorphous group.

2. Hypersthene. Locality: Nain, Labrador. U. S. National Museum No. 93527.

Analysis: Table VIII.

3. Hypersthene collected by C. S. Ross. Not analyzed.

assumption but symmetry relationships and face developments make it improbable. In order to throw further light on the question some of the Espedalen enstatite was heated for several hours at incipient fusion (about 1400°C.). By this heating practically all of the enstatite was converted into typically twinned clino-enstatite. The resulting powder photo-

TABLE VIII. Chemical Analyses of the Enstatite and Hypersthene Minerals Examined by X-rays.

Composition	Espedalen Enstatite	Nain Hypersthene
SiO,	57.28	51.81
$TiO_2$	0.05	o.76
$Al_2O_3$	0.90	2.16
$\mathrm{Fe_2O_3}$	0.42	4.52
FeO	6.43	13.96
MnO	trace	0.16
$_{ m MgO}$	34.94	24.57
CaO	0.13	1.95
$\mathrm{Na_2O}$	0.22	0.39
$K_2O$	0.01	0.03
$H_2O+$	0.13	0.16
Analyst:	Washington	Washington
Reference:	Am. Min. 8, 63 (1923)	Am. Min. 8, 63 (1923)

graph was enough different from that of the original enstatite to make it seem probable that enstatite and clino-enstatite are two separate modifications of MgSiO<sub>3</sub>. It is improbable, however, that the pattern obtained from this decomposed enstatite is that of pure clino-enstatite uncontaminated by enstatite or other crystalline substance. At elevated temperatures diopside and clino-enstatite form an apparently continuous series of solid solutions.7 Powder photographs of these solutions, taken at room temperatures, give what appear to be the mixed patterns of diopside and enstatite. The hypothesis that clinoenstatite can invert to enstatite on cooling and that its solid solutions in diopside unmix with the production of enstatite when cooled does not conflict with any of our X-ray observa-Much more work would, however, be required to show the optical changes involved and what is the actual relation between enstatite and clino-enstatite and the nature of their apparent solid solutions with diopside at low temperature.

Taking the mean of six Espedalen enstatite films as unity, the average spacing ratio from four Nain hypersthene photographs is 0.998. Since the two minerals are sensibly different only in their Mg: Fe" ratio, it would appear that in the enstatite structure the effective volume of ferrous iron atoms is nearly the same as that of magnesium atoms. The hypersthene collected by Ross gave the rather surprisingly large average spacing ratio of 1.010. An analysis of this material would be of considerable interest in showing what substituted atoms are capable of producing this increase in spacing.

### WOLLASTONITE GROUP.

The particular minerals which were found to give powder photographs of the wollastonite type are stated in Table IX.

TABLE IX. Wollastonite-like Minerals Examined by X-rays.

- Wollastonite. Locality: Diana, New York. Specimen not analyzed.
- Pectolite. Locality: Weehawken, N. J. U. S. National Museum No. 80868. Exact composition unknown.
- Schizolite. Locality: Kangerdluarsuk, Greenland. U. S. National Museum No. 93043.
- 4. Bustamite from E. V. Shannon. Composition unknown.

<sup>&</sup>lt;sup>7</sup> N. L. Bowen, this Journal, 38, 207, 1914.

The average spacing for pectolite is not very different from that of wollastonite (0.994 as compared to unity for wollastonite). The other minerals are, however, quite widely different, the ratio being 0.981 for schizolite and 0.979 for bustamite. A small unit cell would have been predicted for these minerals from the smaller effective volumes of manganese than of calcium atoms in such compounds as the oxides and carbonates. Schizolites similar to the one used here have contained as high as 14 per cent. MnO; the manganese content of the bustamite is undoubtedly still greater.

## RHODONITE GROUP.

The X-ray powder photograph of rhodonite is very much poorer than from any of the preceding groups. Series of films made from two samples of rhodonite have been measured. One of these came from Franklin Furnace, the other was from Paisberg in Sweden (U. S. National Museum No. 47426). The composition of neither specimen is accurately known. If the average spacing ratio of the Franklin Furnace rhodonite is taken as unity, that of the Paisberg material is found to be 1.001. According to existing analyses of rhodonites from these two localities their chief impurity is lime.

## MISCELLANEOUS PYROXENE MINERALS.

Powder photographs which are indistinguishable from one another have been obtained from artificial PbSiO<sub>3</sub> and from an alamosite from Alamos, Sonora, Mexico (U. S. National Museum No. 86660). Photographs have also been made from spodumene, from pyroxmangite and from a sample of sobralite. None of these photographs resembles any other nor any of the preceding pyroxene types. Photographs have been made from several samples of babingtonite. The last patterns do not resemble the ones furnished by any of the pyroxene minerals with the possible exception of wollastonite. Though there are certain discernible resemblances between photographs of babingtonite and wollastonite, they are not sufficiently striking for it to be clear whether they have any fundamental significance or are merely affairs of chance.

Many of the calculations of this paper were made by Elizabeth B. Derby.

## SUMMARY.

From an examination of their X-ray powder diffraction photographs it is shown that with the exception of clino-enstatite, babingtonite, spodumene, pyroxmangite, alamosite and sobralite (each of which has a pattern unlike any other) all of the different kinds of minerals usually grouped amongst the pyroxenes have the structure of either diopside, enstatite, wollastonite or rhodonite.

From measurements of several typical augites, which in structure are like diopside, it is seen that the excess ferric oxide and alumina have no clearly marked effect on the X-ray diffraction pattern. Density calculations, combined with the X-ray spacing measurements, prove that these oxides cannot be present in the molecules in addition to the diopside-like constituent; they do not, however, distinguish between the possibility (1) of fine-grained admixture of the oxides themselves<sup>8</sup> or of some other ferric iron and aluminum compounds, or (2) of some sort of atomic replacement involving these oxides.

Comparative spacing measurements of minerals of known chemical composition show that in these pyroxenes ferrous iron replaces magnesium with practically no change in shape or size of the resulting crystal. Manganese in the divalent condition seems to have a slightly larger and calcium a much larger effective volume than these two metals.

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<sup>&</sup>lt;sup>8</sup> Fine-grained hematite should impart a redder color than is observed.