

*The section CaSiO<sub>3</sub>-MgSiO<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>.*

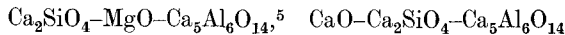
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[Read 22 March 1956.]

*Summary.*—Phase relationships in the section CaSiO<sub>3</sub>-MgSiO<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> through the quaternary system CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> have been determined. The bearing of the results on the genesis of aluminous pyroxenes and associated minerals in metamorphic rocks is discussed.

**A**<sup>N</sup> investigation into the solid solution limits of alumina in the diopside-clinoenstatite series of pyroxenes<sup>2</sup> gave an opportunity to determine some of the phase relationships in the interior of the quaternary system CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. A considerable amount of work has now been done on this system, so that a good picture of the equilibrium relationships is being built up. Results of work on the following parts of the system have been or are being published: anorthite-forsterite-silica,<sup>3</sup> åkermanite-gehlenite,<sup>4</sup>



with 5 % MgO,<sup>6</sup> pseudowollastonite-åkermanite-gehlenite,<sup>7</sup> pseudowollastonite-anorthite-diopside,<sup>8</sup> gehlenite-spinel,<sup>9</sup> diopside-forsterite-anorthite,<sup>10</sup> sections with 5 %, 10 %, 15 %, 20 %, 25 %, 30 % Al<sub>2</sub>O<sub>3</sub>,<sup>11</sup> Ca<sub>2</sub>SiO<sub>4</sub>-Mg<sub>2</sub>SiO<sub>4</sub>-Ca<sub>5</sub>Al<sub>6</sub>O<sub>14</sub>.<sup>12</sup>

<sup>1</sup> The greater part of this work was done whilst the author was a research student in the Dept. of Mineralogy and Petrology, University of Cambridge.

<sup>2</sup> E. R. Segnit, *Min. Mag.*, 1953, vol. 30, p. 218.

<sup>3</sup> Olaf Andersen, *Amer. Journ. Sci.*, 1915, ser. 4, vol. 39, p. 407.

<sup>4</sup> J. B. Ferguson and A. F. Buddington, *ibid.*, 1920, ser. 4, vol. 50, p. 131.

<sup>5</sup> W. C. Hansen, *Journ. Amer. Chem. Soc.*, 1928, vol. 50, p. 2155.

<sup>6</sup> H. F. McMurdie and Herbert Inasley, *Journ. Res. Nat. Bur. Stand.*, 1936, vol. 16, p. 467.

<sup>7</sup> E. F. Osborn and J. F. Schairer, *Amer. Journ. Sci.*, 1941, vol. 239, p. 715 [M.A. 8-258].

<sup>8</sup> E. F. Osborn, *ibid.*, 1942, vol. 240, p. 751 [M.A. 9-16].

<sup>9</sup> R. W. Nurse and N. Stutterheim, *Journ. Iron and Steel Inst.*, 1950, vol. 165, p. 137.

<sup>10</sup> E. F. Osborn and D. B. Tait, *Amer. Journ. Sci.*, 1952, Bowen vol., p. 413 [M.A. 12-81].

<sup>11</sup> E. F. Osborn, R. C. DeVries, K. H. Gee, and H. M. Kraner, *Journ. Metals*, 1954, vol. 6, p. 33.

<sup>12</sup> E. R. Segnit and J. H. Weymouth, unpublished work.

The section pseudowollastonite-clinoenstatite-alumina, the subject of this paper, cuts through the centre of the four-component system from the  $\text{Al}_2\text{O}_3$  apex and includes the compositions of the ternary compounds diopside  $\text{CaMgSi}_2\text{O}_6$ , grossular  $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ , and pyrope  $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ . Its position in the tetrahedron and its relation to other mineral compounds is shown in fig. 1.

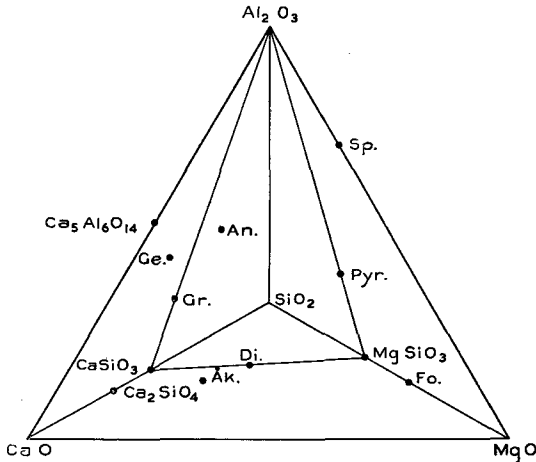
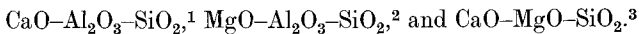


FIG. 1. The quaternary system  $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$  showing the position of the plane  $\text{CaSiO}_3\text{-MgSiO}_3\text{-Al}_2\text{O}_3$  and of the ternary compounds mentioned in the text. Ak, åkermanite; An, anorthite; Di, diopside; Fo, forsterite; Ge, gehlenite; Gr, grossular; Pyr, pyrope; Sp, spinel.

Many of the results on the diopside-clinoenstatite-alumina part of the system were kindly made available by Professor Penkti Eskola of the University of Helsinki, and these have been incorporated. Data on the three boundaries of the section were obtained from the three ternary systems through which they pass:



*Experimental.* For all the experimental work the standard methods of the Geophysical Laboratory, Washington, were used.<sup>4</sup> Sources of  $\text{CaO}$ ,  $\text{MgO}$ , and  $\text{Al}_2\text{O}_3$  were calcium carbonate, magnesium oxide, and aluminium oxide of analytical reagent quality. Crushed rock-crystal

<sup>1</sup> G. A. Rankin and F. E. Wright, Amer. Journ. Sci., 1915, ser. 4, vol. 39, p. 1.

<sup>2</sup> G. A. Rankin and H. E. Merwin, *ibid.*, 1918, ser. 4, vol. 45, p. 301.

<sup>3</sup> J. B. Ferguson and H. E. Merwin, *ibid.*, 1919, ser. 4, vol. 48, p. 81.

<sup>4</sup> G. A. Rankin and F. E. Wright, *loc. cit.*

washed in hydrochloric acid was the source of silica. These compounds were mixed in the requisite proportions and fused in platinum crucibles three to five times with intermediate crushings until homogeneous. The final glasses were crystallized by heating at about  $1000^\circ\text{C}$ . for several

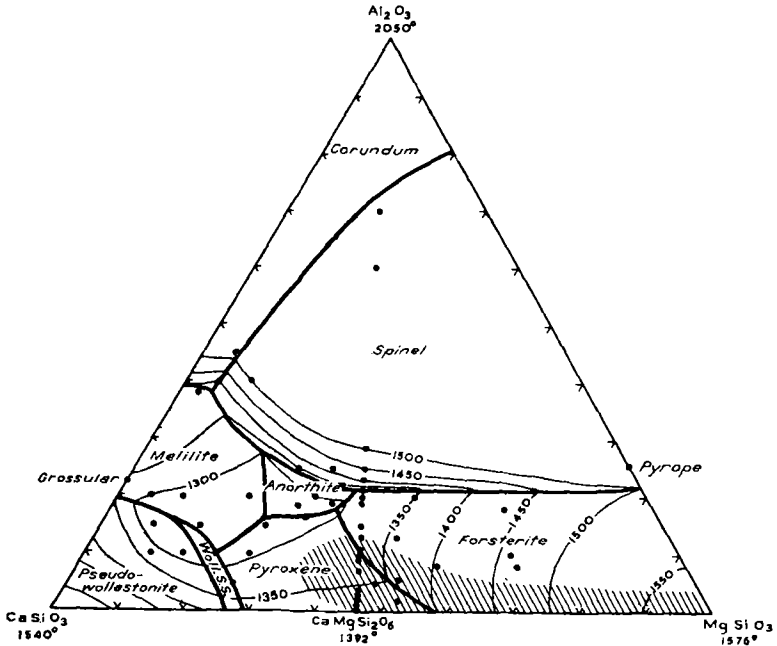


FIG. 2. The section  $\text{CaSiO}_3\text{-MgSiO}_3\text{-Al}_2\text{O}_3$  showing primary phase fields, liquidus isotherms, pyroxene solid solutions, and compositions studied.

hours. The resulting finely crystalline material was then examined by the quenching method.

*Results.* The eight primary phase volumes of corundum, spinel, melilite, anorthite, wollastonite, pseudowollastonite, pyroxene, and forsterite are intersected by the section. All of these phases are well known; their appearance in the quenched charges of this work was as follows: *corundum*, large, thin hexagonal plates; *spinel*, small octahedra; *anorthite*, very thin rhomb-shaped plates, the only crystalline phase in the section with its refractive index lower than that of the embedding glass; *melilite*, rectangular crystals frequently showing square cross-sections; *pseudowollastonite*, large crystals sometimes showing hexagonal cross-sections, high birefringence; *wollastonite*,

poorly formed rounded crystals, refractive index close to that of the embedding glass; *forsterite*, well-formed orthorhombic crystals showing dome faces; *pyroxene*, somewhat oval-shaped crystals with birefringence decreasing with increasing  $MgSiO_3$  and alumina content.

Results of quenching experiments are given in tables I and II. Fig. 2 depicts the primary phase fields and liquidus isotherms derived from the results in tables I and II.

TABLE I. Quenching results along the diopside-alumina join.

Diopside, %	Temp. ° C.	Phases observed.†	Diopside, %	Temp. ° C.	Phases observed.†
99*	1384.5	Gl	85*	1334	Gl
	1384	Gl, Py		1269	Gl, Fo
98*	1379	Gl		1256	Gl, Fo, Py
	1377	Gl, Py		1244	Gl, Py
97*	1370	Gl	83*	1252	Gl, Fo
	1369	Gl, Py		1244	Gl, Py
96*	1363	Gl	81*	1309	Gl
	1361	Gl, Py		1303	Gl, Fo
92.84*	1336	Gl		1242	Gl, Py, Fo?
	1333	Gl, Py		1218	Gl, Py
90.52*	1321	Gl	80	1332	Gl
90	1331	Gl, sm.Py		1291	Gl, Fo
	1313	Gl, Py, Fo	79*	1309	Gl
89*	1325	Gl		1301	Gl, Fo
	1321	Gl, Fo	77*	1350	Gl, Sp
	1300	Gl, Fo	75	1458	Gl
	1291	Gl, Py		1443	Gl, sm.Sp
87*	1333	Gl, sm.Fo		1320	Gl, Sp
	1291	Gl, Fo		1307	Gl, Sp, An
	1283	Gl, Fo, Py	71.24*	1515	Gl
	1275	Gl, Py		1495	Gl, Sp
			40*	1600	Gl, Sp
			30*	1600	Gl, Sp

\* Determined by P. Eskola.

† Gl = glass, Py = pyroxene, Fo = forsterite, Sp = spinel, An = anorthite, sm. = small amount of.

*Glasses.* All the compositions prepared formed glasses on cooling the crucibles in water. Those richer in alumina frequently formed glasses on cooling in air, and occasionally on cooling slowly in the furnace. Refractive indices of the glasses did not vary greatly. They increased with the lime content from approximately 1.58 to nearly 1.63. A diagram of isofracts was published in a previous paper.<sup>1</sup>

*Discussion.* The section behaves as a ternary system only over the

<sup>1</sup> E. R. Segnit, loc. cit.

small areas of the pyroxene,  $\text{CaSiO}_3$ , and corundum fields. Over the rest of the area of the section equilibrium is quaternary. Crystallization paths of compositions outside of the solid solution areas must pass out of the section and end at a quaternary invariant point. Points at which three solid phases are in equilibrium with liquid are not invariant points, but are points of the section pierced by quaternary univariant lines. At temperatures well below the solidus the area of the section which behaves as a ternary system is probably larger owing to the stability range of the garnets being reached.

One of the most striking features of the diagram is the great extent of the spinel field. It indicates that spinel can occur as the primary phase in certain compositions containing as little as 2 %  $\text{MgO}$ . The relatively small field for anorthite suggests that this phase volume will disappear altogether with a further small decrease in silica content of melts outside of the section.

The join diopside-alumina is not a true binary system. At the extreme ends it will act as such, but over the greater part of its length spinel and forsterite are the first phases to crystallize. Under equilibrium conditions mixtures with up to 13 %  $\text{Al}_2\text{O}_3$  will crystallize as homogeneous pyroxene, this being the limit of solid solution of alumina in that phase.<sup>1</sup> Compositions between 11 and 13 %  $\text{Al}_2\text{O}_3$  have forsterite as primary phase, which under equilibrium conditions will react with the liquid to form pyroxene as the temperature falls. The final product will be all pyroxene solid solution. Compositions from 13 to 21 %  $\text{Al}_2\text{O}_3$  also have forsterite as their primary phase; this again reacts with the liquid to form pyroxene, crystallization finishing outside the section. A diagram showing the liquidus and some of the sub-liquidus relations along part of the join is given in fig. 3.

In the low-alumina part of the section is a large solid solution area of alumina in the diopside-clinoenstatite series of pyroxenes (shaded area, fig. 2). Under equilibrium conditions, all compositions within this field will crystallize as homogeneous pyroxene.

This section of the system  $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$  has a number of petrologic applications. It covers the field of aluminous pyroxenes of the diopside-clinoenstatite series, and contains the compositions of several of the most important minerals of thermally metamorphosed carbonate rocks, notably the assemblage diopside-grossular-wollastonite.

The aluminous pyroxenes of this section have been discussed at some

<sup>1</sup> E. R. Segnit, loc. cit.

TABLE II.

Results of quenching experiments in the section  $\text{CaSiO}_3\text{--MgSiO}_3\text{--Al}_2\text{O}_3$ .

$\text{CaSiO}_3$ %	$\text{MgSiO}_3$ %	$\text{Al}_2\text{O}_3$ %	Temp. ° C.	Phases observed.†
The pyroxene field.				
46.4*	51.6	2.0	1386	Gl
			1381	Gl, Py
48.3	46.7	5.0	1359	Gl
			1346	Gl, Py
			1323	Gl, Py, Fo
70.0	25.0	5.0	1321	Gl
			1310	Gl, sm.Py
			1301	Gl, Sp, Wo
65.0	25.0	10.0	1279	Gl
			1265	Gl, Py
			1239	Gl, Py, Wo
60.0	25.0	15.0	1265	Gl
			1260	Gl, Py
53.5	30.1	16.4	1257	Gl, Py
The forsterite field.				
26.7*	69.3	4.0	1480	Gl
			1462	Gl, Fo
44.61*	49.54	5.85	1363	Gl
			1359	Gl, Fo
37.7*	54.3	8.0	1407	Gl
			1403	Gl, Fo
25.6*	66.4	8.0	1471	Gl
			1455	Gl, Fo
25.1*	64.9	10.0	1327	Gl, Fo
			1312	Gl, Fo, Py
			1256	Gl, Fo, Py
41.2*	45.8	13.0	1372	Gl
			1355	Gl, Fo
22.8*	59.2	18.0	1438	Gl
			1430	Gl, Fo
35.0	45.0	20.0	1344	Gl, Fo
The corundum field.				
55.0	5.0	40.0	1406	Gl, sm.Cor
			1381	Gl, Cor, sm.Sp
			1361	Gl, Cor, Sp, An
50.0	5.0	45.0	1520	Gl, Cor
			1464	Gl, Cor
			1423	Gl, Cor, Sp

TABLE II (continued).

$\text{CaSiO}_3$ %	$\text{MgSiO}_3$ %	$\text{Al}_2\text{O}_3$ %	Temp. ° C.	Phases observed.†
The pseudowollastonite field.				
75.0	15.0	10.0	1291	Gl
			1283	Gl, sm. $\psi$ -Wo
			1263	Gl, $\psi$ -Wo
80.0	10.0	10.0	1321	Gl
			1310	Gl, $\psi$ -Wo
77.0	8.0	15.0	1259	Gl
			1249	Gl, $\psi$ -Wo
			1239	Gl, $\psi$ -Wo
			1222	Gl, $\psi$ -Wo, Mel
The anorthite field.				
53.4	27.8	18.8	1270	Gl
			1259	Gl, An
			1183	Gl, An, Py
48.0	33.0	19.0	1289	Gl
			1285	Gl, An
			1269	Gl, An, Fo
50.0	30.0	20.0	1291	Gl, An
			1229	Gl, An, Py
The melilite field.				
70.0	20.0	10.0	1296	Gl
			1291	Gl, sm.Mel
			1288	Gl, Mel, Py
70.0	15.0	15.0	1262	Gl
			1249	Gl, Mel, Wo
60.0	20.0	20.0	1257	Gl
			1244	Gl, Mel
70.0	10.0	20.0	1257	Gl, sm.Mel
			1244	Gl, Mel
75.0	5.0	20.0	1296	Gl, sm.Mel
			1288	Gl, Mel, sm.An
59.0	3.0	38.0	1374	Gl
			1372	Gl, Mel, sm.An
			1366	Gl, Mel, An
The spinel field.				
21.7*	56.3	22.0	1438	Gl
			1426	Gl, Sp
45.0	33.0	22.0	1368	Gl
			1353	Gl, sm.Sp
			1311	Gl, Sp, An
			1285	sm.Gl, Sp, An, Fo
45.0	30.0	25.0	1343	Gl, Sp
50.0	25.0	25.0	1344	Gl, Sp
50.0	10.0	40.0	1450	Gl, Sp

\* Determined by P. Eskola.

† Gl = glass, Py = pyroxene, Fo = forsterite, Cor = corundum, Wo = wollastonite,  $\psi$ -Wo = pseudowollastonite, An = anorthite, Mel = melilite, Sp = spinel, sm. = small amount of.

length in a previous paper.<sup>1</sup> It is now possible, therefore, to draw certain inferences concerning the occurrence and associations of aluminous diopsides. The diopside-spinel join is on the silica-poor side of the  $\text{CaSiO}_3\text{-MgSiO}_3\text{-Al}_2\text{O}_3$  plane and will pass through part of the solid solution volume. This join, however, is not a true binary system. This

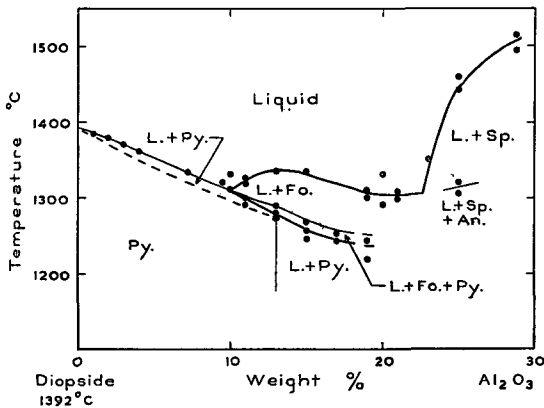


FIG. 3. Some liquidus and sub-liquidus relationships along part of the line diopside-alumina.

is evident from the work of Osborn *et al.*<sup>2</sup> The join pierces their 15%  $\text{Al}_2\text{O}_3$  plane of the quaternary system in the forsterite field. Also, the pyroxene and spinel volumes do not appear to touch at any place, so that the pure compounds cannot co-exist with liquid. This is not in agreement with observations on natural rocks, where pyroxene-spinel assemblages are well known. C. E. Tilley,<sup>3</sup> for example, has published analyses of aluminous pyroxene and spinel from two diopside-spinel assemblages; the pyroxenes in each case contained over 7%  $\text{Al}_2\text{O}_3$ . There are two possible explanations of this discrepancy: the fields of stability of the two compounds may come together at sub-solidus temperatures; and in the natural assemblages a small amount of  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$  is present, which may affect the positions of the phase fields. The spinel-diopside join is never very far from the spinel and diopside boundaries when in the forsterite phase volume; it is possible, therefore, that the  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$  (and possibly other constituents) present in natural pyroxene and spinel may shift the phase boundaries enough to

<sup>1</sup> E. R. Segnit, loc. cit.

<sup>2</sup> E. F. Osborn, R. C. DeVries, K. H. Gee, and H. M. Kraner, loc. cit.

<sup>3</sup> C. E. Tilley, *Geol. Mag.*, 1938, vol. 75, p. 81 [M.A. 7-181].



make the join sensibly binary. Assuming that either or both of these explanations hold, any composition on or near this line will have its equilibrium products controlled by a binary system with considerable solid solution at the pyroxene end. The resulting assemblage would therefore be aluminous diopside-spinel with little or no other phases.

On the  $\text{SiO}_2$  side of the  $\text{CaSiO}_3\text{-MgSiO}_3\text{-Al}_2\text{O}_3$  plane in the region of the diopside-alumina join, compositions close to the binary join anorthite-diopside are encountered. A small amount of silica over that needed for an aluminous diopside can probably be absorbed into the pyroxene structure. That is, the composition is still in the solid solution volume. The join diopside-anorthite, which makes a relatively small angle with the base of the quaternary system, passes through a part of the solid solution volume which takes in pyroxenes with only a low content of  $\text{Al}_2\text{O}_3$ . Pyroxenes in a diopside-plagioclase assemblage should therefore tend to be less aluminous. The steeper diopside-spinel join on the other hand will pass through a greater distance of the solid solution volume and through a part embracing pyroxenes of much higher  $\text{Al}_2\text{O}_3$  content. This is in agreement with the opinions expressed by Tilley in connexion with natural pyroxenes. He also points out that the diopside-alumina join lies in the plane diopside-anorthite-spinel, so that diopside-alumina mixtures up to 48.5 %  $\text{Al}_2\text{O}_3$  may be expressed as a mixture of diopside, anorthite, and spinel. However, spinel could not be expected to appear along this line until the alumina content was rather high. A re-examination of a series of powder photographs of diopside-alumina mixtures taken for the previous paper showed no spinel lines amongst those of diopside and anorthite up to mixtures containing 30 %  $\text{Al}_2\text{O}_3$ , the maximum photographed. Small amounts of spinel are probably present at this stage, but not in sufficient amount to be recorded on a powder photograph.

The composition of grossular appears on the  $\text{CaSiO}_3\text{-Al}_2\text{O}_3$  side of the section (figs. 1 and 2). For the conditions under which grossular is stable there would have to be a join diopside-grossular, and the composition triangle diopside-grossular-wollastonite. Both these assemblages are well known in thermally metamorphosed carbonate rocks. The temperature and pressure conditions under which this equilibrium can be reached in the diagram is not definitely known. Yoder<sup>1</sup> has recently investigated the stability relations of grossular, and his work indicates that low temperatures (of the order of 750° C. and lower for hydrogrossular) are probably more important than high pressures for the formation of this

<sup>1</sup> H. S. Yoder, Journ. Geol., Chicago, 1950, vol. 58, p. 221 [M.A. 11-197].

garnet. High pressures, however, would probably assist its formation. The assemblage diopside-grossular-wollastonite will therefore be represented by a sub-solidus composition triangle in the section  $\text{CaSiO}_3\text{-MgSiO}_3\text{-Al}_2\text{O}_3$ . The join diopside-grossular passes through part of the solid solution field of diopside, so that a small area of solid solution exists in the diopside-grossular-wollastonite triangle. The maximum  $\text{Al}_2\text{O}_3$  content of any pyroxene in this triangle is 5 %, so that, in general, we would not expect diopsides of these parageneses to contain much alumina. This appears to be commonly the case. A diopside separated from a diopside-grossular rock from Norway (Dept. Min. Petr. Cambridge, Spec. 26010), for example, analysed:  $\text{SiO}_2$  53.76,  $\text{Al}_2\text{O}_3$  1.46,  $\text{Fe}_2\text{O}_3$  0.90,  $\text{FeO}$  2.12,  $\text{CaO}$  25.69,  $\text{MgO}$  15.92, total 99.85. In contrast to this it must, however, be noted that analyses of high-alumina diopsidic pyroxenes associated with garnet have been published.<sup>1</sup>

The composition of the magnesian garnet pyrope occurs on the  $\text{MgSiO}_3\text{-Al}_2\text{O}_3$  side of the diagram. The diopside-pyrope join passes through a large part of the solid solution area of diopside, so that it could be possible for the omphacites of eclogites to contain some of their alumina in the tetrahedral groups. Alderman<sup>2</sup> records six analyses of omphacites from eclogites. These pyroxenes contain from 1.13 to 7.01 % of alkalis, thus allowing most of the alumina content to replace (Mg,Fe) in the Y group. In two of the analyses, however, there is still a surplus of a third to a fifth of the total alumina (amounting to approximately 2 %  $\text{Al}_2\text{O}_3$  in the mineral) which must be replacing silicon in the tetrahedral groups.

*Acknowledgements.*—The author desires to record his appreciation of the assistance given in this work by Professor C. E. Tilley, and of the helpful discussion with Professor P. Eskola, as well as his permission to use some of his results in this paper.

<sup>1</sup> J. Kratzert, *Centr. Min.*, 1922, p. 561.

<sup>2</sup> A. R. Alderman, *Quart. Journ. Geol. Soc.*, 1936, vol. 42, p. 488.