Some data on synthetic aluminous and other pyroxenes.

By E. R. Segnit, M.Sc., Ph.D.[1]

Department of Mineralogy and Petrology, University of Cambridge.

[Read January 11, 1951.]

ALTHOUGH detailed experimental investigations have been carried out on the lime, magnesia, and ferrous pyroxenes, relatively little attention has been devoted to synthetic studies of the group involving replacements by ions of higher valencies. In the present study, determinations have been carried out on the limits of solid solution of alumina in pyroxenes in the system $CaSiO_3$–$MgSiO_3$–Al_2O_3. Determinations of the solubility of ferric oxide and titania in diopside were also made.

Experimental procedure.

Pure calcium carbonate, magnesia, silica (crushed and washed rock-crystal), alumina, ferric oxide, and titania were used for the preparation of the mixtures. The constituents in their requisite proportions were fused together four or five times with intervening crushing of the quenched glass. The product was an homogeneous glass free from crystalline material. Homogeneity and composition were checked by refractive index observations under the microscope. These have been plotted in figs. 1 and 2. Fig. 1 shows the effect of added alumina, ferric oxide, and titania (wt. %) on the refractive index of diopside glass, and fig. 2 indicates the variation in refractive indices of glasses in the system $CaSiO_3$–$MgSiO_3$–Al_2O_3.

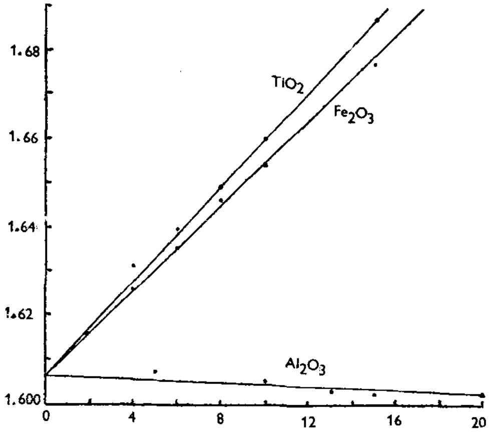

Fig. 1. Graph of refractive indices against composition of diopside glasses containing other oxides.

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[1] Now at Division of Industrial Chemistry, Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia.

To determine the limits of solid solution, the glasses were crystallized by heating below their solidus temperatures for periods varying from two hours to several days. The shorter periods were generally sufficient for complete crystallization. If the product was in the solid-solution field, only one phase would be visible under the microscope. If it was outside the field, a second, generally crystalline, phase would appear. In some cases, several days' heating was insufficient to crystallize the glass completely. This happened with some of the more aluminous glasses and was taken as evidence of inhomogeneity. X-ray powder photographs were also used as a check on homogeneity, but were not as sensitive as microscopic examination.

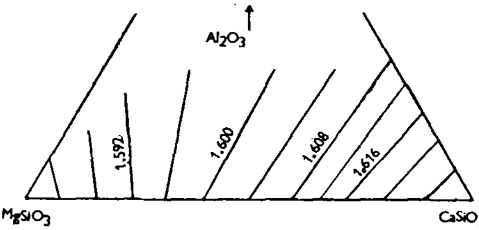

FIG. 2. Refractive indices of glasses in the system $CaSiO_3$–$MgSiO_3$–Al_2O_3. Lines at intervals of 0·004 of refractive index.

EXPERIMENTAL RESULTS.

High magnification showed that the crystallized products were either granular or fibrous in structure. In the latter case, with compositions lying outside of the solid-solution field, the second phase formed in parallel growth with the pyroxene.

The result of this microscopic examination is shown in fig. 3. The area within the curve represents the solid-solution limits of alumina in the pyroxenes in the system $CaSiO_3$–$MgSiO_3$–Al_2O_3. Glasses with compositions lying in this area will crystallize as a single pyroxene phase at temperatures below their solidus. The most precise determinations were made in the area close to diopside. Three series of compositions were prepared along lines joining diopside to alumina, and to the compositions represented by 'MAS' and 'CAS'.[1] The limits of solid solution along these lines were placed at:[2]

Diopside	87%	Al_2O_3	13%
,,	75	CAS	25
,,	80	MAS	20

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[1] For the sake of simplicity in more complex formulae, the following abbreviations have sometimes been used in this paper: C = CaO, A = Al_2O_3, M = MgO, S = SiO_2.

[2] A. I. Zvetkov, Mém. Soc. Russe Min., 1945, ser. 2, vol. 74, pp. 215-222 [M.A. 11-92] has reported mixed crystals on the join diopside–$CaAl_2SiO_6$ containing up to 18-19 wt. % Al_2O_3.

Away from this area the solubility of alumina fell off rapidly to about 5 % along the main part of the diopside clinoenstatite series. The data in this part of the series is not as precise, owing to the high melting points, which caused some difficulties in the preparation of satisfactory glasses. The presence of minute air bubbles and vesicles also added to the difficulties of determination of homogeneity. Clinoenstatite glasses containing 5 % and 2·5 % Al_2O_3 were, however, prepared. When crystallized, the former was inhomogeneous, while the latter was almost quite homogeneous. A small lowering of the refractive index of the crystals also confirmed that the clinoenstatite was taking some alumina into solid solution. At the other end of the solid-solution area may be noted the small part beyond the diopside–CAS join. Here, there must be a small excess of the large calcium ion in the structure.

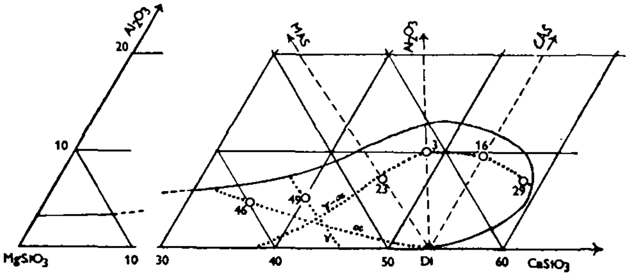

FIG. 3. Pyroxene solid solutions in the system $CaSiO_3$–$MgSiO_3$–Al_2O_3. Glasses within the curved line crystallize as a single phase. Dotted lines show refractive indices α 1·664, γ 1·690, and birefringence γ—α 0·025.

A few determinations were also made of the limits of solid solution of ferric oxide and titania in diopside. Glasses were prepared at 2 % intervals along the diopside–oxide join to the limit of 10 % of each oxide, and a further glass with 15 % of Fe_2O_3. These were then subjected to the same treatment as the aluminous mixtures. In this manner the limits for homogeneous crystallization in the two cases were found to be diopside 94 % with titania 6 %, and diopside 90 % with Fe_2O_3 10 %. Larger, although inhomogeneous crystals were obtained by slow cooling from the melt. These were useful for the qualitative determination of the effect of the various oxides on the optic axial angle, extinction, and dispersion.

OPTICAL PROPERTIES OF THE ARTIFICIAL PYROXENES.

The refractive indices and other properties are summarized in table I. Refractive indices were measured on fine material obtained by the crystallization of glasses. The optic axial angles and extinction angles were measured on ground mounts of coarse inhomogeneous crystals obtained by slow cooling from the melt. The optic axial angle was determined with the universal stage.

TABLE I. Optical properties of pyroxene solid solutions.

Aluminous:

		Composition.				
No.[1]	$CaSiO_3$.	$MgSiO_3$.	Al_2O_3.	α.	γ.	γ−α.
3	48·3	41·7	10·0 %	1·668	1·693	0·025
16	53·5	37·0	9·5	1·669	1·694	0·025
23	45·6	46·9	7·5	1·669	1·695	0·026
29	58·5	34·5	7·0	1·670	1·695	0·025
46	35·0	60·0	5·0	1·664	1·682	0·018
49	40·0	55·0	5·0	1·667	1·690	0·023
Diopside (artificial)				1·664	1·694	0·030

Ferriferous:

		Diopside.	Fe_2O_3.			
F1	... ...	98·0	2·0 %	1·670	1·702	0·032
F2	... ...	96·0	4·0	1·677	1·705	0·028
F3	... ...	94·0	6·0	1·684	1·710	0·027
F4	... ...	92·0	8·0	1·691	1·716	0·025

Titaniferous:

		Diopside.	TiO_2.			
T1	... ...	98·0	2·0 %	1·667	1·695	0·028
T2	... ...	96·0	4·0	1·677	1·704	0·027

Optic axial angle on coarse material:

Aluminous	76°
Ferriferous	77
Titaniferous	77

Maximum extinction angle on longitudinal section:

Aluminous	43°
Ferriferous	43

[1] Compositions 3–49 plotted in fig. 3.

Diopsides containing alumina.—On the whole, this constituent has very little effect on the optical properties of diopside. The α refractive index is slightly raised, while γ is unaffected, the net result being to decrease the birefringence by about 0·005 in the highly aluminous members. The birefringence of pure diopside is 0·030; this is lowered to 0·025 by the addition of about 10 % alumina. In contrast to this, alumina lowers slightly the refractive index of the corresponding glass. In fig. 3 the pyroxenes with a birefringence of 0·025 are indicated by a dotted line. There was little change in the extinction angle, but there was an increase of about 16° in the optic axial angle. It is evident that alumina does not cause any characteristic change in the optical properties by which its presence could be accurately diagnosed or determined quantitatively.

Diopsides containing titania.—The effect of titania is more marked than that of alumina. The refractive indices of diopside are increased by about 0·004 for each per cent. of TiO_2, and at the same time there is a similar decrease in the birefringence, as was seen in the aluminous pyroxenes. The optic axial angle was increased to about 77°. This is of particular interest because it has been suggested that titanium causes a considerable drop in the optic angle measurement. The above result is direct evidence that TiO_2 cannot be the cause of low optic axial angle in some titaniferous pyroxenes. The synthetic material is colourless.

Diopsides containing ferric oxide.—The changes in optical properties were similar to those noticed with titania. The refractive indices were increased. γ increases about 0·003 for each per cent. of Fe_2O_3, α at a slightly greater rate, so that there is a decrease of about 0·005 in the birefringence of the members rich in iron. The optic axial angle was increased to about 77°. The colour of the iron-rich members is striking —a strong orange-brown in section. The preparation with only 2 % Fe_2O_3 had only a slight greenish tint under the microscope. All varieties were practically non-pleochroic. The dispersion was strong $r > v$, and was striking in near optic axis sections.

STRUCTURAL REPLACEMENT IN THE PYROXENES.

B. E. Warren and J. Biscoe (1931) suggested as a general formula for pyroxenes $X_m Y_{2-m}(Si,Al)_2(O,OH,F)_6$, where m tends to be unity or zero, and as much as one quarter of the silicon may be replaced by aluminium. In this formula X = Ca, Na, K, or Mn, and Y = Mg, Fe, Al, Ti, or Mn. In simple pyroxenes there is no difficulty in placing the various elements in their respective places in the structure. Divalent elements should replace each other in the X and Y groups according to their ionic radii. Alkalis should go into the X group and the valencies balanced by the replacement of divalent elements in the Y group by aluminium or ferric iron as in the jadeite and acmite molecules. The position becomes more complex, however, if the latter oxides are present and alkalis are not, as is the case with these synthetic materials and also with many natural minerals. The three replacements in the synthetic materials will be now considered.

Alumina.—Although the ionic radius of aluminium (0·57 Å.) is greater than that of silicon, it can replace the latter in the oxygen tetrahedron as is well known in the felspar structure. When diopside, therefore, takes alumina into solid solution, the valencies are balanced by half of the new constituent going into the *Y* group to replace magnesium (ionic radius 0·78 Å.), and the other half in with the silicon group. The overall result should be a small decrease in cell size. The introduction of the larger aluminium ion into the rigid oxygen tetrahedron should not affect this part of the structure, while the replacement of magnesium by aluminium in the more loosely bound part of the structure should tend to cause a slight decrease in the cell dimensions. This result was shown by a series of powder photographs of diopside–alumina mixtures. With increase in alumina content an increase in the line spacings denoting a decrease in cell size was evident on visual inspection.

Ferric oxide.—The same remarks may be applied to this constituent as were applied to alumina. The ferric ion should in part replace silicon, and in part the *Y*-group metal, in this case magnesium. There can be little objection to the replacement of silicon by the ferric ion, as its ionic radius (0·67 Å.) is only a little greater than that of aluminium. The limit of solid solution should therefore be more restricted; and this has been confirmed by synthetic work. The ferric and magnesium ions are of similar size, so that powder photographs of iron-rich synthetic diopsides showed no alteration in cell size. That the ferric ion can enter into the oxygen tetrahedron has been shown by G. T. Faust (1936), who proved the existence of the iron-orthoclase molecule.

Titania.—The position which titanium takes up in any structure depends upon the valence of that particular titanium ion. In natural minerals titanium is usually reported as the dioxide TiO_2, although E. Dittler (1929) suggests that it may sometimes occur as Ti_2O_3. He was able, under suitable conditions, to prepare synthetic silicates and other compounds in which trivalent titanium occurred. It is unlikely, however, that such conditions could ever occur in nature. This is especially so in the case of pyroxenes, because those which are rich in titanium are also rich in ferric oxide. That Fe_2O_3 and Ti_2O_3 could coexist under any conditions of elevated temperature is most improbable. It can be safely assumed that the dioxide is present in pyroxenes, and can as such replace silica to a small extent. The synthetic work showed this limit to be about 6 %, which is comparable to the amount of ferric iron which enters into the oxygen tetrahedron (half the total amount of Fe_2O_3 soluble in diopside, which was determined as 10 %). This also follows from the similar ionic sizes of titanium and trivalent iron. Furthermore, no increase in cell size can be expected and the powder photographs showed no change.

Similar conclusions were reached by T. F. W. Barth (1931), who obtained comparable results with some synthetic work. He held preparations of 94 % $CaMgSi_2O_6$ with 6 % $CaMgTi_2O_6$ and of 90% $CaMgSi_2O_6$ with 10 % $CaMgTi_2O_6$ at 1300° C. for two hours and obtained homogeneous crystals. The latter composition contains about 6 % TiO_2, thus being in agreement with the present results. In all these artificial materials, titanium must occur in the silicon group although in natural pyroxenes rich in alumina it may preferably replace magnesium, the valence being balanced by the replacement of silicon by aluminium.

NATURAL PYROXENES RICH IN ALUMINA, FERRIC OXIDE, AND TITANIA.

Pyroxene analyses are common in the literature, and a large number of the igneous varieties have been collected and published in tables by P. Niggli (1943). These constitute the majority of the reliable analyses of igneous pyroxenes. Metamorphic pyroxenes are less common. In this work, interest is centred on those which have a low alkali content; 76 such analyses, taken chiefly from Niggli's tables, together with a number of metamorphic pyroxenes (C. E. Tilley, 1938), have been recalculated as percentages of $CaSiO_3$, $(Mg,Fe,Mn)SiO_3$, and $(Al,Fe)_2O_3.TiO_2$. Fig. 4 shows a plot of these analyses on a diagram corresponding to fig. 3. Most of the natural minerals lie within the experimental field, and a survey of those lying outside the field shows that these are titania rich. If the titania were subtracted from the total $Al_2O_3+Fe_2O_3+TiO_2$ and added in with the silica, these analyses would fall within the synthetic curve. The one or two exceptions to this will be mentioned below.

Two theoretical probabilities which could be drawn from the above experimental results are confirmed by the plot of analyses in fig. 4. They are, firstly, that the total of alumina+ferric oxide in a pyroxene is unlikely to exceed the maximum amount of solid solution possible for alumina itself, and, secondly, that this limit will not be appreciably affected by ferrous oxide replacing magnesia. Many of the pyroxenes plotted in fig. 4 are rich in FeO. Titania may be able to increase the total amount of high valence oxides as its replacement of silica is of a somewhat different type.

There are several published analyses which do not agree with the above results. In each case there are unusual factors, but without further study no decisive conclusions can be reached. The most notable examples are the titanaugite from Aberdeenshire with over 24 % $Al_2O_3+Fe_2O_3+TiO_2$ which is uniaxial (B. E. Dixon and W. Q. Kennedy, 1933), an augite from Cap Tourmente, Quebec, with 24 % $(Al,Fe)_2O_3$ and little titania (H. M. Putman, 1942), a titanaugite from Siberia with 8·97 % TiO_2 (P. I. Lebydev and A. P. Lebydev, 1934), and two peculiar pyroxenes obtained from artificial rock melts (J. Morozewicz, 1898), one of which contains over 39 % $Al_2O_3+Fe_2O_3+TiO_2$.

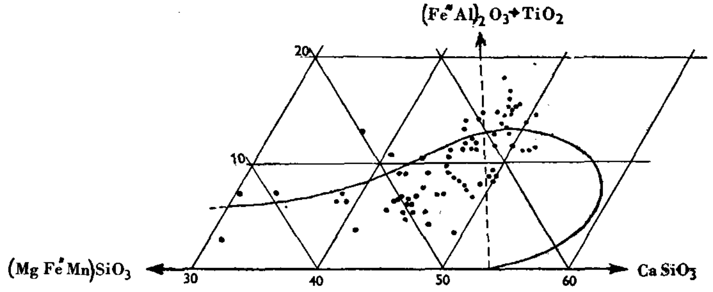

Fig. 4. Curve of fig. 3 and 76 natural pyroxenes in part of the triangle $CaSiO_3$–$(Mg,Fe,Mn)SiO_3$–$(Fe,Al)_2O_3+TiO_2$. (Pyroxenes with low $(Fe,Al)_2O_3+TiO_2$ not plotted.)

The optical properties of the artificial materials did not show any significant changes which might be used for identification purposes. A comparison with analysed natural pyroxenes is in harmony with this. Of the group of minerals with which this work is concerned, there is no consistent change of properties which could not be attributed to changes caused by replacements among the divalent elements. The decrease in birefringence noticed in the synthetic pyroxenes is reflected in the natural minerals. This seems to be a characteristic effect of the entrance of Fe_2O_3, Al_2O_3, and TiO_2, and has been confirmed by H. H. Hess (1949). This particularly applies to alumina, which causes no appreciable change in properties. Mauve-coloured pyroxenes are often referred to as titanaugites, but not all proved titaniferous augites are of this colour.

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