Aluminium replacing silicon in some silicate lattices.

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THE purpose of this account is to review, from the literature, figures for the replacement of silicon by aluminium in biotites, calciferous amphiboles, and clinopyroxenes. Atomic ratios to be quoted have been calculated on a basis of 24(O,OH,F) in biotites, hornblendes, and pyroxenes alike. This facilitates comparison and the higher factor magnifies differences. It may be emphasized, to avoid possible confusion, that in this discussion it is the amount of silicon replaced by aluminium that will be under review. The ratio of tetrahedrally co-ordinated Al to octahedrally co-ordinated Al will not be considered, although for the sake of completeness, figures for Al in *Y* groups will be furnished to show total Al values. Machatschki's group notation is employed. Comparison between biotites, hornblendes, and clinopyroxenes, for present purposes, may best be made between minerals that crystallized under the same pressure-temperature conditions, to reduce variables. Few analyses of specimens of these three minerals, that have crystallized together in the same rock, are available however. One such paragenesis is quoted below. This association occurs as gneiss-like inclusions in calcite, taken from the Tiree marble.[1]

		Pyroxene.	Hornblende.	Biotite.
Z ...	Si	7·468	6·14	5·56
	Al	0·532	1·86	2·44
Y ...	Al	0·284	0·89	0·52

Despite the lack of information regarding such associations from the same rock, comparison between biotite, hornblende, and clinopyroxene may be made when those minerals have crystallized during the orthomagmatic stage of plutonic igneous activity. Their conditions of formation will then have been approximately similar. The following average values for igneous biotite have been taken from Nockolds.[2]

The atomic ratios of silicon and aluminium in the *Z* group of magmatic hornblendes varies largely within the limits Si 6·40, Al 1·60 and Si 5·60,

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[1] A. F. Hallimond, Min. Mag., 1947, vol. 28, p. 230.

[2] S. R. Nockolds, Amer. Journ. Sci., 1947, vol. 245, p. 401. [M.A. 10–271.]

Average values for biotites from calc-alkaline plutonic rocks.

	Associated mineral ...	Topaz.	Muscovite.	Biotite alone.	Hornblende.
Z ...	Si	5·89	5·30	5·49	5·53
	Al	2·11	2·70	2·51	2·47
Y ...	Al	1·42	0·78	0·38	0·15

Average values for biotites from alkaline plutonic rocks.

	Associated mineral...	Biotite alone.	Alkali-amphibole.	Aegirine.
Z ...	Si	5·48	5·63	5·52
	Al	2·52	2·37	2·48
Y ...	... ...	0·44	0·05	—

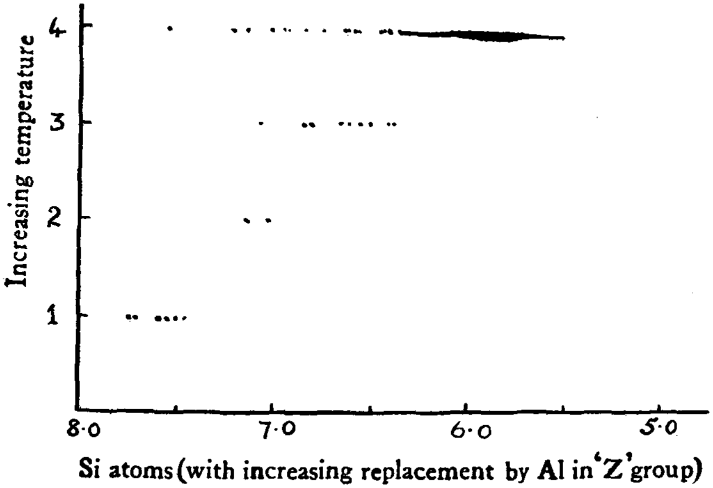

FIG. 1. Plot of hornblende analyses from: 1, green-schist metamorphic facies; 2, albite-epidote-amphibolite facies; 3, amphibolite facies; 4, igneous rocks.

Al 2·40. There is, however, a decline in the number of magmatic hornblende analyses showing values for aluminium substitution in the *Z* group exceeding the ratio Si 6·00, Al 2·00. These general relations are exemplified by fig. 1, in which the atomic ratios of silicon in these amphiboles are plotted on a horizontal line. Isolated dots on this line indicate individual analyses. Where the dots representing the latter become too closely spaced to permit differentiation they are represented as a solid line, thickest where the analyses are most abundant. The data have largely been selected from 196 igneous and metamorphic calciferous amphiboles quoted by Hallimond.[1]

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[1] A. F. Hallimond, Amer. Min., 1943, vol. 28, p. 65. [M.A. 9–270.]

The magmatic pyroxenes have been recently discussed by Niggli.[1] Representative values for plutonic clinopyroxenes are quoted below.

		I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
Z	Si ...	7·56	7·588	7·200	7·288	7·332	7·140	7·468	7·344	7·448	7·340
	Al ...	0·44	0·412	0·800	0·712	0·668	0·860	0·532	0·608	0·552	0·660
Y	Al ...	0·07	0·160	0·048	0·108	0·240	0·172	0·580	—	0·332	0·116

I. S. R. Nockolds and R. L. Mitchell, *Trans. Roy. Soc. Edinburgh*, 1948, vol. 61, p. 560. [M.A. **10**–424.]

II–III. S. R. Nockolds, Geol. Mag., 1938, vol. 75, p. 469. [M.A. **7**–304.]

IV–X. L. R. Wager and W. A. Deer, Medd. Grønland, 1939, vol. 105, no. 4. [M.A. **8**–27.]

I is taken from peridotite, the rest from gabbroic rocks.

The biotites, hornblendes, and pyroxenes cited have all been selected from plutonic rocks. The composition of a mineral as crystallization proceeds and temperature declines may reflect one or both of two factors, the stability requirements of the lattice and the composition of the magma. Rapidly crystallizing minerals may form metastable phases, however, in which case the control exerted by lattice requirements may be wholly eliminated. Ratios for minerals taken from effusive rocks have therefore been omitted.

It will be seen above that the degree to which aluminium replaces silicon in the biotites, calciferous amphiboles, and clinopyroxenes of igneous plutonic rocks is characteristic for each mineral group. Further, this replacement value is greatest in the biotites, of intermediate magnitude in the amphiboles, and least in the pyroxenes.

Comparisons may now be made between the members of one mineral group to investigate the manner in which the degree of Si–Al substitution varies with different physical conditions of crystallization. For such a purpose the calciferous amphiboles are admirably suited, possessing a wide field of chemical stability and persisting as stable minerals from the green-schist facies to the amphibolite facies, the latter being widespread in regional metamorphic terrains. Moreover, passage between the two facies is a normal sequence in progressive metamorphism and appears to be dominantly controlled by rising temperatures, thus simplifying the discussion in terms of operative physical variables. The effect of rising temperatures upon Si–Al substitution in the calciferous amphiboles may be seen from the following atomic ratios for calciferous amphiboles taken from the green-schist facies, epidote-albite-amphibolite facies, and the amphibolite facies. These hornblendes comprise the vast majority of the rock-forming amphibole varieties. Those amphiboles

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[1] P. Niggli, Schweiz. Min. Petr. Mitt., 1943, vol. 23, p. 538.

omitted from discussion, cummingtonite, grunerite, and the glaucophanes, are unusual species, often occurring in parageneses of doubtful significance.

Amphiboles from the green-schist metamorphic facies.

		I.	II.	III.	IV.	V.	VI.
Z	Si ...	7·743	7·734	7·591	7·610	7·537	7·474
	Al ...	0·257	0·244	0·409	0·406	0·463	0·526
Y	Al ...	0·193	0·022	0·189	0·053	0·206	0·127

I–II. From hornblende-epidote-albite-schist, South Devon. C. E. Tilley, Geol. Mag., 1938, vol. 75, p. 497. [M.A. 7–446.]

III. From hornblende-talc-chlorite-schist, South Devon. C. E. Tilley, ibid.

IV. From chlorite-epidote-albite-amphibolite, Argyll. J. D. H. Wiseman, Quart. Journ. Geol. Soc., London, 1934, vol. 90, p. 354. [M.A. 6–224.]

V. From albite-stilpnomelane-actinolite-schist. C. O. Hutton, Mem. Geol. Surv. New Zealand, 1940, no. 5. [M.A. 8–19.]

VI. From albite-epidote-actinolite-calcite-schist. C. O. Hutton, ibid.

Amphiboles from the epidote-albite-amphibolite facies.

		I.	II.
Z	Si ...	7·160	7·062
	Al ...	0·840	0·938
Y	Al ...	0·562	0·547

I. From garnet-biotite-epidote-albite-amphibolite. J. D. H. Wiseman, ibid.

II. From biotite-epidote-albite-amphibolite. J. D. H. Wiseman, ibid.

Amphiboles from the amphibolite facies.

		I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Z	Si ...	6·69	6·63	6·40	7·10	6·41	6·82	6·59	6·52
	Al ...	1·01	1·37	1·60	0·90	1·59	1·18	1·41	1·48
Y	Al ...	—	0·97	0·57	0·62	0·48	1·30	0·86	0·11

I. L. Duparc and F. Pearce, Bull. Soc. Franç. Min., 1908, vol. 31, p. 118.

II. S. Tsuboi, Japanese Journ. Geol. Geogr., 1936, vol. 13, p. 333. [M.A. 7–30.]

III. A. Marchet, Tschermak's Min. Petr. Mitt., 1925, vol. 38, p. 500. [M.A. 3–82.]

IV, and V. T. Du Rietz, Sveriges Geol. Undersök., 1938, Ser. C, no. 416, p. 70. [M.A. 8–235.]

VI. L. Hezner, Tschermak's Min. Petr. Mitt., 1903, vol. 22, p. 562.

VII. P. Eskola, Vid.-Selsk. Skr., I. Math.-nat. Kl., 1921, vol. 1, no. 8. [M.A. 2–313.]

VIII. A. W. Groves, Quart. Journ. Geol. Soc. London, 1935, vol. 91, p. 158.

The first seven of these examples were taken from amphibolites. VIII is from charnockite in which the amphiboles represent adjustments to the amphibolite facies. VI and VII are derived from altered eclogites.

The figures given indicate that with rising metamorphic temperatures silicon in the *Z* group of the calciferous amphibole structure is progressively replaced by aluminium. In this connexion it is interesting that among the examples taken from the green-schist facies, numbers V and VI, which for the hornblendes cited from that facies are richest in tetrahedrally co-ordinated aluminium, were taken from rocks in Hutton's 'chlorite 4 sub-zone' near the top of the facies. Amongst those specimens cited from the amphibolite facies, number IV, with the smallest amount of aluminium in substitution for silicon, is a pale-coloured variety in contact and intimate association with mica-schist and occurring with appreciable amounts of chlorite. It appears to represent a lower metamorphic grade than is shown by the other hornblendes in the amphibolite facies table. The amount of tetrahedrally co-ordinated aluminium in the metamorphic calciferous amphiboles appears then to be a direct function of the temperature at which crystallization took place at equilibrium.

Hornblendes with greater values for Al in Si–Al substitution, than shown by those cited, have been recorded from metamorphic rocks in the amphibolite facies. Two such are given below:

		I.	II.
Z ...	Si ...	6·19	6·13
	Al ...	1·81	1·87
Y ...	Al ...	0·52	1·07

I was taken from a garnet-amphibolite, Glenelg[1] and II from a kyanite-amphibolite, Glenelg.[2] Such highly aluminous hornblendes customarily belong to parageneses of doubtful interpretation in which the chemistry of the parent-rock appears to have considerably influenced the nature of the hornblende. Both examples cited are of eclogitic parentage, deriving from omphacite.

Comparison between the two groups of hornblendes, the igneous and metamorphic, may now be made. Their relations are shown in fig. 1. Of 118 calciferous amphiboles cited by Hallimond[3] showing Si–Al ratios in the *Z* group between the limits Si 8·00, Al 0·00 and Si 6·40, Al 1·60, only 33 were taken from igneous rocks. Of these only 13 (chiefly from diorites) may perhaps be accepted as stable under orthomagmatic conditions, the other 20 having either been modified under sub-magmatic conditions or else occurring in lava types in which case they may be in disequilibrium, as discussed. For hornblendes with values for aluminium substitution higher than Si 6·40, Al 1·60 the proportion of igneous to metamorphic hornblende increases rapidly, until the latter are excluded

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[1] A. R. Alderman, Quart. Journ. Geol. Soc. London, 1936, vol. 92, p. 519.

[2] C. E. Tilley, Min. Mag., 1937, vol. 24, p. 565.

[3] A. F. Hallimond, Amer. Min., 1943, vol. 28, p. 65. [M.A. 9–270.]

for Si values less than 5·90. Passage from metamorphic to magmatic conditions appears to take place in the calciferous amphibole series with increase in aluminium replacing silicon.

A further relevant point is raised by the following data, taken from Nockolds and Mitchell,[1] and Deer.[2]

Average values for hornblendes from some Caledonian plutonic rocks.

		I.	II.	III.
Z ...	Si ...	6·31	6·79	7·12
	Al ...	1·69	1·21	0·88
Y ...	Al ...	0·22	0·11	0·15

I. Average values of 5 early hornblendes in appinitic types.

II. Average values of 6 primary hornblendes in diorites and trondjhemites.

III. Average values of 4 late crystals from various chemical environments.

Of group III Nockolds and Mitchell suggest that all hornblendes in that group may be the products of late solutions altering pre-existing pyroxenes and primary amphiboles. The figures demonstrate a decrease in the amount of aluminium substituting silicon with declining temperature of formation. Within the calciferous amphiboles the proportion of tetrahedral aluminium therefore apparently increases from the lowest metamorphic grade to the field of magmatic activity. The amount of tetrahedral aluminium within this group appears to reflect the temperature of formation of different species and may perhaps be used with due care as a geological thermometer and aid in discussion of facies within the range of normal progressive metamorphism. The increasing entry of alumina into calciferous hornblende with increasing metamorphic grade is well known, and is exemplified by the passage: pale amphibole—blue-green hornblende—common green hornblende—brown hornblende (magmatic). To the best of the writer's knowledge, however, no one has yet drawn attention specifically to the function of tetrahedrally co-ordinated aluminium atoms.

In discussion, a point has occasionally been made in recent years of the fact that passage from one member of Bowen's discontinuous reaction series to another member of the series takes place by fundamental changes in the atomic configurations of the minerals concerned. Progressing from low to higher temperature members of the series, sheet

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[1] S. R. Nockolds and R. L. Mitchell, Trans. Roy. Soc. Edinburgh, 1948, vol. 61, p. 560. [M.A. **10**–424.]

[2] W. A. Deer, Min. Mag., 1938, vol. 25, p. 56.

lattices (e.g. biotite) are succeeded in turn by double-chain structures (amphiboles), single-chain arrangements (pyroxenes), and isolated tetrahedral units (olivines). In a reaction pair, transformation to the higher-temperature member is effected by the severance of certain bonds binding the tetrahedral units together. By such bond breakages infinite tetrahedral sheets (e.g. micas) may eventually be reduced to individual tetrahedra. Since reactions in the direction mica → olivine result with rising temperature, the accompanying successive bond breaks may be roughly conceived as taking place largely in response to increased thermal agitation of the lattice. Biotites, hornblendes, and pyroxenes may nevertheless crystallize together in stable equilibrium. Since the figures quoted for Al substitution are greatest in the most complex structure (biotite) and least in the pyroxenes, it may appear that tetrahedrally co-ordinated Al stabilizes the former under physical conditions promoting crystallization of simpler lattice types. The charge ratio between Al and Si in silicate lattices is 3:4. Replacement of Si by Al therefore leaves the oxygens of the tetrahedral units concerned electrostatically unsatisfied. By Pauling's rules, those oxygens tend to enter into bonds with cations external to the tetrahedra. Buerger[1] thus suggests on these grounds that replacement of Si by Al helps to control the stability of a mineral and its position in the reaction series. On such a basis it might also similarly be argued from data cited that Al plays a corresponding stabilizing role in the higher-temperature hornblendes.

However, replacement of Si by Al instead of strengthening the lattice might actually weaken it by reducing the bond strengths within tetrahedra whilst strengthening bonds to cations outside the tetrahedral units. This might favour breakage of Al–O bonds and simplification of the tetrahedral pattern.

Also low values for Si–Al substitution in the clinopyroxenes may be explained in the following manner. In silicate lattices electrostatic balance must be re-established after such exchanges have taken place. This may be achieved with replacement of cations by others of similar radius but higher charge, by 'building-in' of additional cations, or by substitution of O by OH. In pyroxenes only the first case obtains. This necessitates exchange of divalent cations for tervalent cations of similar size. These are rare, and therefore Si–Al substitution values are generally small in pyroxenes. In the biotites, however, the Mg positions seem narrow and can accommodate smaller tervalent ions like Fe^{3+}. Also

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[1] M. J. Buerger, The rôle of temperature in mineralogy. Amer. Min., 1948, vol. 33, pp. 101–121. [M.A. 10–380.]

univalent K can be replaced, and O is possibly replaceable by OH. The biotite micas may therefore attain considerable Si–Al substitution values, whilst in hornblendes substitution is assisted by the presence of 'vacant positions'. Lastly, Niggli[1] has pointed out that, in magmas, the co-ordination value of Al may be determined by the amount of volatiles present. This idea has been developed by von Eckermann.[2]

With regard to the data from calciferous hornblendes; these appear to furnish another case of the general rule that, in any one mineral, the higher the temperature of formation, the higher the solid solubility of any element. The high-temperature hornblendes are therefore richest in aluminium.

As a final note, it is interesting to compare the habits of low-grade actinolitic amphiboles with those of igneous hornblendes. The latter tend to form stout stumpy prisms, whilst the former are generally of columnar, bladed, or asbestiform habit. Possibly this reflects the amount of tetrahedrally co-ordinated aluminium in each. Low values for Si–Al replacement, such as obtain in the actinolitic amphiboles, may be argued to result in weaker binding between chains of tetrahedra, favouring asbestiform developments. A high degree of replacement of silicon by aluminium, as in the magmatic hornblendes, then would favour strong links between chains and a stumpy prismatic habit. Alternatively, it may be suggested that high values for Al substitution of Si weaken the oxygen bonds binding tetrahedra into chains, therefore hinders extension of the latter during crystallization, and thus favours a stumpy form.

Acknowledgements.—The writer wishes to thank Dr. J. E. Richey for acting as communicator, Professor S. J. Shand and Dr. H. Neumann for reading the manuscript.

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[1] P. Niggli, Das Magma und seine Produkte. Leipzig, 1937. [M.A. 7–2.]

[2] H. von Eckermann, Geol. För. Förh. Stockholm, 1944, vol. 66, p. 283.