Amphiboles from the Younger Granites of Nigeria. Part I. Chemical classification.

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Summary. The Younger Granites of Nigeria contain varied assemblages of iron-rich ferromagnesian minerals in which amphiboles are an important component. Eighteen of these amphiboles (separated from rocks belonging to nine complexes) have been chemically analysed and the results are presented and discussed. The amphiboles are shown to fall into two groups, a lime-alkali group (comprised of ferrohastingsite of general formula $NaCa_2Fe''_4Fe'''Al_2Si_6O_{22}(OH)_2$) and an alkali group (of general formula $(Na, K, Ca)_{2.5-3.0}(Fe'', Fe''')_5(Al, Si)_3O_{22}(OH)_2$). The alkali amphiboles are characterized by their extremely low magnesia content, by the presence of Li and F (both in significant amounts), and are of special interest because of the unusual amount of ZnO they contain. Optical properties of the amphiboles have been determined but it has not been found possible to use these properties to determine accurately the chemical composition of the alkali amphiboles. It is suggested that, according to current classifications of amphiboles, the analysed alkali amphiboles should be called riebeckitic arfvedsonites or arfvedsonites. The relationship between the hastingsites and the alkali amphiboles is not yet clear.

ALTHOUGH a great deal of research has been carried out on the granitic ring-complexes of Northern Nigeria, no systematic study has been made of variations in the chemical composition, optical properties, and structure of the different groups of their ferromagnesian minerals, and in particular of the large group of iron-rich alkali and calc-alkali amphiboles, which are associated with fayalite, pyroxene, and biotite. This paper deals mainly with the alkali amphiboles—riebeckitic arfvedsonite and arfvedsonite—but a small number of calc-alkali amphiboles of hastingsite composition are discussed briefly (the latter will be dealt with more fully in a future paper).

The Younger Granites occur throughout an area of 25 000 square miles in the Northern Region of Nigeria. About forty of these complexes have been found and a large number mapped in detail; some are intrusive into the Pre-Cambrian basement complex and most are of uncertain age.[1] Many show a partial or, less commonly, a complete ring structure and may have a number of intrusive phases present, belonging both to

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[1] Darnley *et al.* (1962) give a mean age of 159 ± 25 m.y. to fergusonites from two different localities in the Jos area of Northern Nigeria.

volcanic and granitic cycles of activity, but this complete cycle of volcanic and granitic rocks is not always present and a number of 'complexes' may consist of a single intrusion only. Mapping of these complexes has been carried out over many years by a number of workers, and the results of the more recent research have been summarized by Jacobson, Macleod, and Black (1958), who give a number of mineral analyses. The petrography of several riebeckite-granites has been dealt with by Beer (1954).

Previous work on alkali and calc-alkali amphiboles. As the occurrence of the iron-rich end-members of these two groups of amphiboles is not frequently reported from igneous rocks and as the literature dealing with these minerals is rather scattered, it seems relevant to make a brief mention of previous work on these two amphibole groups.

Riebeckite ($Na_2Fe''_3Fe'''_2Si_8O_{22}(OH, F)_2$). Sauer (1888) first recognized that the mineral present in granitoid rocks from Socotra was an amphibole, and he named it riebeckite. The analysis of the Socotra riebeckite shows it to be extremely rich in ferric (28·30 %) compared with ferrous-iron (9·87) and the Fe''/Fe''' ratio (atomic) is < 0.5, compared with a ratio of 1·5 for the theoretical end-member; a re-analysis of the Socotra mineral would seem desirable. Other analyses of igneous riebeckites include those of Palache and Warren (1911), Lacroix (1922), and Chapman and Williams (1935). More recent analyses have been given by Miyashiro and Miyashiro (1956), Sabine (1960), and Garson (1960). Analyses of three Nigerian riebeckites were given by Jacobson *et al.* (1958) and these analyses are comparable with those of the present author.

Arfvedsonite   ($Na_2Ca_{0.5}Fe''_{3.5}Fe'''_{1.5}Al_{0.5}Si_{7.5}O_{22}(OH)_2$

or $Na_3Fe''_4Fe'''Si_8O_{22}(OH)_2$).

Early analyses of arfvedsonite include those by Eskola and Sahlstein (1930) and by Iwao (1939) and these authors also discussed the abnormal optical properties of the mineral. Yagi (1953) analysed the arfvedsonite from the alkaline rocks of Morotu District, Sakhalin. Sundius (1946) dealt with solid solution relations in the amphiboles (calciferous and alkali), and the chemistry, optics, and genesis of the alkali amphiboles have also been discussed by Miyashiro (1957).

Hastingsite ($NaCa_2(Fe'',Mg)_4(Fe''',Al)Al_2Si_6O_{22}(OH)_2$). The first attempt to discuss the chemistry, optics, and genesis of the hastingsite group in a systematic way was made by Billings (1928), who suggested three subdivisions based on the atomic ratio Fe''/Mg'': ferrohastingsite

with $Fe''/Mg > 2$, femaghastingsite with $Fe''/Mg > 0.5 < 2$, and magnesiohastingsite with $Fe''/Mg < 0.5$. A large number of analyses of hastingsite (the iron-rich members) have been made including a number quoted by Billings (1928). More recent analyses have been given by Buddington and Leonard (1953), Miyashiro and Miyashiro (1956), and Compton (1958).

Granitic rocks of the Nigerian complexes and their petrography. Granitic rocks of the ring complexes have been described under three main headings (Jacobson *et al.*, 1958): biotite granites, riebeckite granites, and amphibole–fayalite granites. The riebeckite granites are usually described as riebeckite, aegirine–riebeckite, riebeckite–biotite, or albite–riebeckite granites, but it should be emphasized that the number and kind of ferromagnesian minerals to be found in an intrusion of any one of these rock types appears to vary slightly in different parts of the same intrusion. The amphibole–fayalite granites include hornblende–biotite, arfvedsonite, and pyroxene–fayalite granites and porphyries. Only the granites relevant to this paper are described here.

Modal analyses and localities of the granites are given in table I. Modes were determined with a Point Counter using three slides of each granite and making 5000 counts (on average) according to the texture of the particular rock. Where possible only discrete grains were included under 'albite' although a great deal of albite may be visible in the perthite, which is always the dominant feldspar, and which is sometimes a microcline-perthite; most of the plagioclase appears to be of albite composition. The colour index of many of the rocks is low.

The riebeckite granites. Although the texture, the amount of albite present, and the distribution of dark minerals vary considerably from section to section and from rock to rock, the most important features can be summarized:

A small number of the riebeckite granites, R.4, R.5, and R.6 from Sara-Fier, are medium- to coarse-grained rocks with abundant perthite of vein type, which shows very little evidence of unmixing to albite or of replacement by the latter. Riebeckite is sparsely developed and may be found interstitially or as feathery aggregates of very small crystals of late formation and the mineral may be zoned or twinned. No aegirine is present. In R.11 from Amo the riebeckite may occur as small late interstitial grains or as elongate ragged grains, but there is a great deal of replacement albite present and the texture is less uniform than that of the previous group of riebeckite granites.

Several of the rocks, R.2 and R.3 from Liruei, R.7, R.8, and R.9

from Shere Hills, R.10 and R.11 from Kigom Hills, and R.15 from Buji, contain aegirine and riebeckite. These rocks vary considerably in grain size and (grain) texture and in the degree of exsolution and albite replacement that they show. The relative proportions of riebeckite: aegirine are also variable; in R.3 they are approximately 1:1; in R.9 there is very little aegirine, and in the others the ratio riebeckite:aegirine is 2 or 3:1. Both minerals may be of early or late formation, either may act as core to the other (even in the same thin section), or they may form parallel elongate intergrowths and occasionally replace one another. In R.7 large riebeckite crystals are often partly mantled by very small aegirine crystals and small aegirine grains have also formed along fractures in some of the riebeckite grains. Both minerals may be zoned and the riebeckite does not always go into extinction.

R.1 from Liruei and R.14 from Amo show very extensive replacement of all minerals, including riebeckite, by small albite laths. These two rocks also have a number of uncommon accessory minerals—cryolite, pyrochlore, and topaz. The feldspar in R.14 is dominantly microcline-perthite.

Common accessories in many of the granites include astrophyllite, fluorite, allanite, biotite, and zircon. R.10 and R.11 from Kigom Hills also contain ore minerals (including molybdenite, pyrite, chalcopyrite), which are accompanied by calcite.

Arfvedsonite granite. Arfvedsonite occurs in R.16 from Sha-Kaleri, which is a medium-grained rock rich in ferromagnesian minerals. The feldspar is mainly perthite with very little albite, and feldspar and quartz are often intergrown. The arfvedsonite is strongly pleochroic in light browns and bluish greens; the colour is variable and the mineral may be strongly zoned. Some of the arfvedsonite occurs interstitially or as small grains that merge into fibrous aggregates, but a great deal of the mineral occurs, often as partly rounded grains, in clusters of mafic minerals, the latter including serpentine and iddingsite pseudomorphs after fayalite, iron oxide, and remnants of aegirine or other pyroxene; amphibole may occur as a reaction rim around the altered fayalite. A considerable number of small euhedral or sub-hedral grains of aegirine and fayalite pseudomorphs occur enclosed in the perthites, together with small grains of iron oxide and fluorite. An interesting feature of the rock is the number of xenoliths of earlier, often porphyritic, granite that it contains.

Ferrohastingsite granites. Ferrohastingsite has been separated from a number of early intrusions, the modal analyses of which are given in table I.

TABLE I. Modal analyses (vol. %).

	R.1.	R.2.	R.3.	R.4.	R.5.	R.6.	R.7.	R.8.	R.9.	R.10.	R.11.	R.12.	R.13.	R.14.	R.15.	R.16.	R.17.	R.18.	R.19.	R.20.
Quartz	29·9	27·0	34·9	36·4	33·6	31·2	34·7	32·8	32·3	32·6	28·1	36·4	23·4	32·1	28·0	20·1	23·7	1·2	18·5	27·8
Orthoclase and perthite (albite and microcline)	42·7	58·2	62·1	60·1	64·9	62·7	49·9	52·9	56·2	55·9	58·1	53·3	65·5	48·8	50·6	67·2	67·1	79·6	68·7	66·1
Albite	13·3	9·1	1·2	2·6	tr.	0·8	7·4	8·7	7·4	7·4	5·7	7·8	4·3	12·3	5·2	1·9	3·6	11·4	3·6	2·8
Biotite	—	0·3	—	—	—	—	—	tr.	—	—	—	—	—	—	—	—	1·4	—	3·3	1·6
Hornblende	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	3·6	4·5	4·7	1·9
Riebeckite / Arfvedsonite	8·1	2·4	1·8	0·5	1·3	4·6	5·3	4·0	1·6†	2·1	5·8	0·4	6·7	3·8	4·2	7·9	—	—	—	—
Aegirine	1·0	2·9	—	—	—	—	2·2	1·3	—	0·7	1·5	—	—	—	2·8	—	—	—	—	—
Pyroxene	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	2·4*	—	2·2	—	0·1
Fayalite‡	—	—	tr.	—	—	tr.	—	—	—	—	—	1·4	—	—	—	tr.	tr.	tr.	tr.	tr.
Opaque minerals	—	0·3	tr.	—	tr.	tr.	—	—	—	0·7	0·2	—	tr.	—	tr.	0·2	0·1	1·0	0·5	—
Zircon	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0·3	tr.	0·3	tr.	—
Fluorite	—	—	tr.	—	tr.	tr.	—	—	—	—	—	—	—	0·3	—	tr.	—	—	0·5	—
Allanite	—	—	—	—	—	—	—	—	—	—	—	—	—	2·5	—	tr.	—	—	—	—
Pyrochlore	1·2	—	—	—	—	—	—	—	—	—	—	—	—	0·5	—	—	—	—	—	—
Cryolite	3·1	—	—	—	—	—	—	—	—	0·5	0·3	0·3	tr.	—	—	—	—	—	—	—
Topaz	—	—	—	—	—	—	—	—	—	—	0·1	0·4	—	—	—	—	—	—	—	—
Astrophyllite	—	—	—	0·4	tr.	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Calcite	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Epidote	0·5	—	—	—	—	tr.	—	—	—	—	—	—	—	—	—	—	tr.	—	—	—

* Relics of both.
† Includes aegirine.
‡ Rarely present except as relics, usually altered to serpentine, iddingsite, etc.

Key to Tables I–IV

R.1 Albite–riebeckite granite, PB 3. Kaffo Valley, Kiruei complex.
A.1 Amphibole from R.1.
R.2 Aegirine–riebeckite granite, PB 7. Liruei complex.
A.2 Amphibole from R.2.
R.3 Riebeckite–aegirine granite, PB 20. Liruei complex.
A.3 Amphibole from R.3.
R.4 Riebeckite granite, PB 50. Sara-Fier complex.
A.4 Amphibole from R.4.
R.5 Fine riebeckite granite, PB 57. Sara-Fier complex.
A.5 Amphibole from R.5.
R.6 Coarse riebeckite granite, PB 58. Sara-Fier complex.
A.6 Amphibole from R.6.
R.7 Albite–riebeckite granite, PB 63. Near Shere peak, Shere Hills.
A.7 Amphibole from R.7.
R.8 Riebeckite–biotite granite, PB 64. Near Shere peak, Shere Hills.
A.8 Amphibole from R.8.
R.9 Riebeckite–biotite granite, PB 65. Near Shere peak, Shere Hills.
A.9 Amphibole from R.9.
R.10 Albite–riebeckite granite, PB 83. Kigom Hills.
R.11 Albite–riebeckite granite, with molybdenite, PB 84. Kigom Hills.
R.12 Albite–riebeckite granite, with molybdenite, chalcopyrite, and pyrite, PB 85. Kigom Hills.
A.12 Amphibole from R.12.
R.13 Riebeckite granite, PB 30. Amo complex.
A.13 Amphibole from R.13.
R.14 Albite–riebeckite granite, PB 79. Amo complex.
A.14 Amphibole from R.14.
R.15 Albite–riebeckite granite, PB 92. Buji complex.
A.15 Amphibole from R.15.
R.16 Hotum arfvedsonite granite, PB 37. Kaleri complex.
A.16 Amphibole from R.16.
R.17 M'Bul hornblende-fayalite granite, PB 38. Daffo, town, Kaleri complex.
A.17 Ferrohastingsite from R.17.
R.18 Pankshin syenite, PB 48. Pankshin complex.
A.18 Amphibole from R.18.
R.19 Early hornblende–biotite granite. Jos-Bukuru complex. PB 96.
A.19 Amphibole from R.19.
R.20 Early hornblende–biotite granite, PB 97. Jos-Bukuru complex.
A.20 Amphibole from R.20.

In R.18, a medium-grained syenite from Pankshin containing very little quartz and abundant perthite, albite may occur at feldspar grain boundaries and albite twin lamellae are visible in the perthite. The original (grain) texture of the rock has been partly obliterated and boundaries between feldspars are often merely indistinct wavy or sutured lines. Ferromagnesian minerals include interstitial amphibole associated with iron oxide or pseudomorphs after fayalite, and a pale green, probably hedenbergitic, pyroxene (maximum extinction 45°), which appears to be of early formation. Very little ragged biotite occurs. The other ferrohastingsites occur in R.17, a hornblende–fayalite granite from Kaleri, and in R.19 and R.20, both early hornblende–biotite granites from Jos-Bukuru. Both the latter rocks are coarsely perthitic, the feldspar sometimes being intergrown with quartz. Patches of nearly discrete albite grains showing sharp lamellar twinning occur in a number of the perthite grains and albite also appears at feldspar grain boundaries. Pericline twinning is also well developed in the plagioclase of R.20. The biotite is strongly pleochroic from dark brown to nearly colourless; it is commonly interstitial or may occur as trains of ragged grains, less than 1 mm long, in the feldspar. The amphibole is pleochroic in light browns and deep greens and occurs as elongate interstitial grains up to 1·5 mm long, or may occur with biotite in clusters of mafic minerals; the latter include biotite, amphibole in tuft-like aggregates, and iron oxides, associated with patches of very spongy amphibole and sheaves of small biotites. Fluorite, coarse zircons, and acicular grains of apatite are common accessories. The composition of the iron oxide present in these amphibole granites is not known.

Preparation of material for analysis. The analysed amphiboles were separated after crushing to mesh sizes between −70 and −175, and an initial separation of heavy minerals was made using the Frantz Isodynamic Separator, followed by the removal of any remaining quartz and feldspar by centrifuging the heavy fraction in methylene iodide. Considerable difficulty was experienced in the separation of riebeckite from finely intergrown aegirine, and in the separation of amphibole from aenigmatite in R.3, but generally the purity of the final fraction is considered to have been greater than 99 %, the impurities being mainly aegirine, aenigmatite, and astrophyllite.

Analytical methods. Classical gravimetric methods of analysis were used, with 0·5 g to 0·6 g of sample, for SiO_2, MgO, CaO, and total R_2O_3, alumina being determined initially by difference in the usual way. However, for minerals like the alkali amphiboles that have a low alumina and high iron content, the figure obtained for alumina may be in considerable error, due to the presence of platinum and

zirconia and the possibility that zinc and lead (present in many of the Nigerian amphiboles) may be partially or wholly precipitated with the R_2O_3 and included in the alumina total. For this reason alumina and zirconia were determined separately, as follows: 10 to 25 mg of sample were 'fritted' with Na_2O_2, leached in water, and the solution boiled and filtered. The alkaline filtrate was neutralized and used for the determination of alumina[1] and the residue dissolved in 3 N HCl and used to determine zirconia. Both determinations were made using the colorimetric methods recommended by Sandell (1950, 1959). The double precipitation of magnesium was done at a pH of approximately 11 to ensure that zinc would remain in solution. Colorimetric methods of analysis were used to determine TiO_2, MnO, and P_2O_5, and the alkalis were determined by flame photometer. Lithium was determined spectrographically and by flame photometer (spectrographic determination carried out by I. Nichol, Department of Applied Geochemistry, Imperial College). For the spectrographic determination a synthetic alkali 'amphibole' of composition similar to that of the Nigerian minerals was made up and included 1 % lithium. This synthetic amphibole was used as a standard with which to compare the natural minerals. Comparison of the photometric and spectrographic figures (see table II) shows good agreement. Total iron (as FeO) was determined by titration using the stannous chloride method, and FeO was determined by the ammonium vanadate method described by Wilson (1955). For chlorine, fluorine, and water the methods recommended by Kolthoff and Sandell (1952) were employed. Zinc was determined colorimetrically (after elimination of other interfering trace metals) during trace element analysis using a slightly modified method described by Stanton et al. (1962). Chromium was also determined colorimetrically (on the filtrate used for alumina) but was always below the limit of sensitivity (100 p.p.m.). Where the amount of material available allowed, the amphiboles were also analysed for the trace elements Cu, Co, Ni, and Pb using colorimetric methods. Duplicate or triplicate analyses were made on approximately 0·5 g of material for Ni, Pb, Cu, and Co, the results being satisfactory for Cu and Pb, but less so for Ni. It was generally impossible to estimate Co for most of the minerals because of interference by Zn, but where the amount could be determined it was less than 0·05 p.p.m.

The amphibole formula. Sundius (1946) derived the magnesium-rich end members of the alkali and lime-alkali groups hypothetically by considering substitutions in the tremolite formula $Ca_2Mg_5Si_8O_{22}(OH)_2$ (ferrous analogues are derived by substitutions in the actinolite formula). For the alkali amphiboles the end-member, richterite, is derived by substitution of Na_2 for one Ca atom, which gives a formula $Na_2CaMg_5Si_8O_{22}(OH)_2$ (in this formula the vacant space is filled by Na). By further substitution of Na for Ca, and substitution of Al for Mg in the Y-group to adjust the valences, another end-member, eckermannite, is derived with the formula $Na_3Mg_4AlSi_8O_{22}(OH)_2$, the ferrous analogue being arfvedsonite. If, on the other hand, Na is substituted for Ca in the ratio 1:1 in the tremolite formula without filling the vacant spaces in the lattice, valency adjustment must be made by substitution

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[1] A British Chemical Standards sample of Liberian iron ore, Cat. No. 175/1, was used to check precision in the determination of alumina; alumina was found to be 1·18 % compared with a given value (average) of 1·10 %. Determination of alumina carried out by I.S.E. Carmichael, Department of Geology, Imperial College.

of Al for Mg in the Y-group and this leads to the formula of a third end-member, glaucophane, $Na_2Mg_3Al_2Si_8O_{22}(OH)_2$, the ferrous analogue being riebeckite.

In the calc-alkali amphiboles Sundius derived one end-member, edenite, by filling the vacant position in the tremolite formula with Na and balancing the valences by substitution of Al for Si; this leads to a formula $NaCa_2Mg_5AlSi_7O_{22}(OH)_2$. The other formula for a calc-alkali amphibole which Sundius derived was not considered by him to be that of an end-member as further substitutions are theoretically possible, but he used it as a standard formula: the formula is that of pargasite, $NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2$, which is obtained by substitution of AlAl for MgSi and of NaAl for Si in the tremolite formula, the ferrous analogue being hastingsite.

Miyashiro's (1957) classification differs from that of Sundius in a number of ways, but the most important difference as far as this paper is concerned is in his suggested formula for arfvedsonite, $Na_2Ca_{0.5}Fe''_{3.5}Fe'''_{1.5}Al_{0.5}Si_{7.5}O_{22}(OH)_2$.

Formulae of the Nigerian amphiboles. In the discussion that follows the formula $NaCa_2Fe''_4Fe'''Al_2Si_6O_{22}(OH)_2$ is used for the hastingsite group as being that which most closely reflects the composition of the calc-alkali amphiboles from Nigeria. For the alkali amphiboles, which have a variable composition, the formulae of riebeckite, $Na_2Fe''_3Fe'''_2Si_8O_{22}(OH)_2$, arfvedsonite (after Miyashiro), $Na_2Ca_{0.5}Fe''_{3.5}Fe'''_{1.5}Al_{0.5}Si_{7.5}O_{22}(OH)_2$, and arfvedsonite (after Sundius), $Na_3Fe''_4Fe'''Si_8O_{22}(OH)_2$, have all been used as a basis for discussing the chemical variations in the group studied. All the formulae of the Nigerian minerals have been calculated to 24 $(O+OH+F)$.

Chemistry of the amphiboles from the Younger Granites. Chemical analyses are given in tables II and IV and unit cell formulae in tables III and IV.

Riebeckitic-arfvedsonites and arfvedsonites

The Z-Group includes Si^{4+} (0·42 Å), Al^{3+} (0·51 Å), Ti^{4+} (0·68 Å), and Zr^{4+} (0·79 Å), but even after allotting these ions to this group, most of the alkali amphiboles showed some deficiency in occupancy of the eight possible tetrahedral sites. Therefore, as it seems essential for the tetrahedral positions to be filled, some Fe''' (0·64 Å) has also been included in the Z-group. Reference to table III shows that there is an increase in Si relative to the other quadrivalent ions Zr and Ti, and also an increase in Si relative to Al, the latter varying from 0·21 atoms in A.4 to 0·02

TABLE II. Analyses and optical properties of the alkali amphiboles. For key to these analyses, see p. 363.

	A.1.	A.2.	A.3.	A.4.	A.5.	A.6.	A.7.	A.8.	A.9.	A.12.	A.13.	A.14.	A.15.	A.16.
SiO_2	50.25	48.09	47.45	47.70	47.60	48.59	49.60	48.44	48.74	49.15	48.47	49.61	50.19	47.56
ZrO_2	0.56	0.43	0.28	0.87	0.14	0.20	0.44	0.15	0.13	0.20	0.41	0.21	0.20	0.28
Al_2O_3	0.26	0.60	0.66	1.15	0.86	0.92	0.34	0.10	0.86	0.95	0.59	0.27	0.24	0.88
TiO_2	0.80	1.74	1.61	1.04	1.66	1.28	0.70	1.15	1.17	1.14	0.74	0.52	0.60	1.51
Fe_2O_3	13.95	10.88	12.65	12.90	13.71	13.22	11.48	12.42	12.61	13.10	11.89	12.91	13.34	9.28
FeO	17.09	25.33	21.41	22.57	22.35	21.10	22.24	21.12	21.52	20.60	22.93	19.50	20.53	26.03
Li_2O*	2.20	0.53	0.42	0.52	0.46	0.67	0.51	0.97	0.99	1.16	0.74	1.76	0.65	n.d.
MnO	0.62	0.62	0.98	0.54	0.60	0.47	0.40	0.52	0.41	0.32	0.37	0.48	0.37	0.61
MgO	0.04	0.05	0.03	0.44	0.07	0.03	0.16	0.42	0.05	0.30	0.05	0.13	0.03	0.34
ZnO	0.93	0.43	0.33	0.50	0.59	0.56	0.64	0.62	0.64	0.64	0.47	0.47	0.78	0.26
PbO	0.18	n.d.	n.d.	n.d.	0.01	0.06	0.07	0.04	0.07	0.04	0.01	0.07	0.02	n.d.
CaO	0.20	0.87	2.88	2.22	1.74	1.79	0.90	1.95	1.02	0.64	0.88	0.31	0.49	4.27
Na_2O	8.80	7.41	8.62	6.36	6.92	7.30	8.77	7.92	8.08	7.66	8.88	9.43	8.67	5.74
K_2O	2.20	1.01	1.82	1.14	1.20	1.62	1.70	1.68	1.75	1.96	1.60	1.65	1.89	1.15
P_2O_5	0.16	0.08	0.08	0.07	0.02	0.05	0.04		0.03	0.04	0.01	0.13	0.04	0.20
H_2O+	0.4	1.3	1.7	1.7	1.6	1.4	1.1	1.1	1.3	1.3	1.0	1.1	1.3	1.54
H_2O-	0.09	0.15	0.22	0.12	0.05	0.12	0.06	0.03	0.07	0.10	0.08	nil	nil	0.09
F	3.31	1.03	1.40	1.31	1.4	1.61	2.20	2.33	2.06	2.17	2.20	2.48	2.00	0.56
Cl	0.18	0.12	0.07	0.05	0.09	0.04	0.08	0.01	0.10	0.16	0.03	0.09	0.06	0.40
Total	102.22	100.67	100.61	101.20	101.07	101.03	101.59	101.01	101.10	101.63	101.35	101.12	101.40	100.70
Less O = F, Cl	1.43	0.46	0.61	0.56	0.61	0.69	0.94	0.96	0.88	0.96	0.93	1.06	0.85	0.33
Total *Photometric	100.79	100.21	100.00	100.64	100.46	100.34	100.55	100.05	100.22	100.67	100.42	100.06	100.55	100.37
Trace elements p.p.m.														
Lithium (spec.) As Li_2O	2.16	0.43	0.54	0.32	0.32	0.65	0.86	0.97	0.86	1.3	0.54	1.3	0.65	
Copper	7	n.d.	n.d.	n.d.	7	7½	3	3	7	39	5	8	11	
Nickel	4½	n.d.	n.d.	n.d.	4½	3	4	4½	4½	9½	5	3½	8½	
Lead	1800	n.d.	n.d.	n.d.	114	550	710	374	694	390	85	674	214	
Zinc	7500	3500	2625	4000	4750	4500	5125	5000	5125	5125	3750	3875	6250	
α'	1.677	1.691	1.694	1.692	1.691	1.685	1.676	1.684	1.685	1.681	1.679	1.677	1.677	?1.691
$\gamma'(-\alpha')$	1.693	1.696	1.702	1.704	1.704	1.699	1.688	1.699	1.697	1.700	1.694	1.695	1.698	1.700
$(\gamma'-\alpha')$	0.016	0.005	0.008	0.012	0.013	0.014	0.012	0.015	0.014	0.019	0.015	0.018	0.021	
2V	High	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	?75-80°	n.d.	High	n.d.	n.d.	n.d.	
α:[001]	4°±1°	0°	0°	0°	0°	-3°	ca. 6°	ca. 3°	n.d.	1°±1°	0°	4°±1°	5°±1°	75°±5°
Pleochroism														
α	indigo	deep grn.-blue		deep blue	indigo	deep grn.-blue	indigo	indigo	indigo	indigo	indigo	v. deep blue	indigo	
β	blue	dk. grey-blue		dk. grey-blue	deep blue-grn.	dull blue-grn.	grey blue	dk. grey-blue	dk. blue	dk. grey-blue	deep blue	deep blue	deep grn.-blue	
γ	lt. grn.-yell.	lt. straw		yellowish	dk. yell.-grn.	greenish yell.	lt. yell.-grn.	yell.-grn.	yellowish	yell.-grn.	yell.-grn.	pale grn.-yell.	lt. yell.-grn.	

atoms in A.8. These two variations have been combined and shown graphically in fig. 1. The theoretical line along which the points should lie has also been shown and the scatter of points indicates the amount of Fe''' necessary to bring the atomic total to eight in this group.

The *Y-Group* includes Fe^{2+} (0·74 Å) and its substitutes Li (0·68 Å),
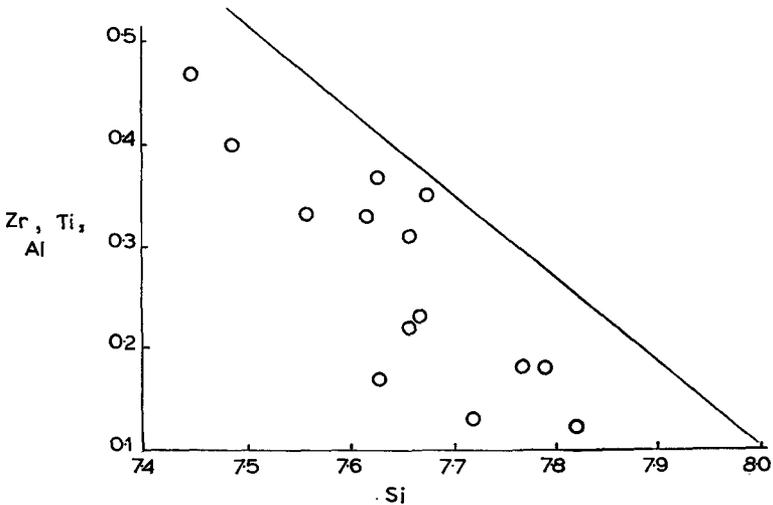
FIG. 1. Atomic variations in Si with other members of the Z-group. Circles represent Nigerian alkali amphiboles.

Mn^{2+} (0·80 Å), Mg^{2+} (0·66 Å), and Zn^{2+} (0·74 Å), together with Fe^{3+} (0·64 Å). A small amount of Na (0·97 Å) has also been included in this group where there is an excess over three atoms in the *X*-group. Na has been included in the *Y*-group in preference to Ca^{2+} (0·99 Å) as it is a slightly smaller ion and because it is probably a later entrant into the lattice than Ca. Of the minor substitutes for Fe'' (Mn, Mg, and Zn), magnesium is of little importance and never amounts to more than 0·11 atoms (in A.4): Mn ranges from 0·04 atoms in A.12 to 0·13 atoms in A.3, but no systematic variation of Mn with Fe'' occurs. The most interesting minor substitution is that of Zn for Fe'' although it never exceeds 0·10 atoms (in A.1). Reports of Zn being present in silicate minerals in significant amount are not very common, the most comprehensive survey being that of Wedepohl (1953), who, however, did not report zinc in amphiboles. Sundius (1946) gives an analysis of eckermannite from Norra Karr, Sweden, that includes 0·59 % ZnO, and Tauson and Kravchenko (1956) have reported the presence of zinc

in hornblendes and biotites from Caledonian granitoids of the Susamin batholith of Central Tian-shan, but the authors considered the possibility of submicroscopic blende being present in the minerals. X-ray work on single crystals by M. Frost of Manchester University has not shown the presence of any zinc compound in the amphiboles being discussed and it seems that the zinc is present as a normal lattice substi-
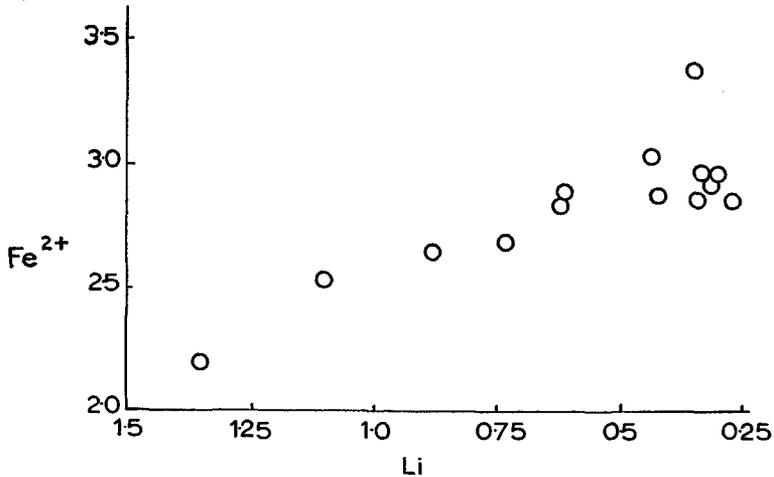
FIG. 2. Atomic variations in Li with Fe″. Circles represent Nigerian alkali amphiboles.

tute for Fe″. In terms of the variation in amount of Fe″ present in the unit cell, the most important substitution is that of Li for Fe″, the amount of Li varying from 0·27 atoms in A.3 to 1·36 in A.1, the latter mineral being very low in ferrous iron. Fig. 2 shows that there is a general increase of Li with decrease of Fe″.

Ferric iron may increase in alkali amphiboles when monovalent ions, Na or K, substitute for Ca, or Li substitutes for Fe″; some ferric iron can then replace Fe″ to maintain the electron balance. In the amphiboles now being considered, reference to table III shows that a slight correlation can be made between variation of Fe‴ and variation of Fe″ and a slight correlation also exists between variation in atomic proportion of Li and changes in the Fe″/Fe‴ ratio. No close correlation can be made between decrease of Ca (in the X-group) and increase of Fe‴.

The X-group includes the large 8-coordinated ions Ca, Na, and K (1·33 Å) and includes any alkali occupying the normally vacant (A)

lattice sites. In addition small amounts of Mn and Fe″ have been included in the group where there is an excess of atoms in the Y-group. A fairly close correlation ought to exist between variation in the amount of the alkali metals present and variation in Ca, and reference to the unit cell formulae in table III shows that such correlation can be made. Although

TABLE III. Formulae of alkali amphiboles calculated to 24 (O+OH+F). For key to these analyses, see p. 363.

	A.1.	A.2.	A.3.	A.4.	A.5.	A.6.	A.7.	A.8.	A.9.	A.12.	A.13.	A.14.	A.15.	A.16.
Si ...	7·77	7·68	7·56	7·49	7·45	7·62	7·79	7·63	7·66	7·66	7·67	7·72	7·82	7·63
Al ...	0·05	0·11	0·12	0·21	0·16	0·17	0·06	0·02	0·07	0·17	0·11	0·05	0·04	0·17
Zr ...	0·04	0·03	0·02	0·07	0·11	0·01	0·03	0·01	0·01	0·01	0·03	0·02	0·01	0·02
Ti ...	0·09	0·18	0·19	0·12	0·20	0·15	0·09	0·14	0·14	0·13	0·09	0·06	0·07	0·18
Fe‴ ...	0·05	—	0·11	0·11	0·08	0·05	0·03	0·20	0·12	0·03	0·10	0·15	0·06	—
Z ...	8·00	8·00	8·00	8·00	8·00	8·00	8·00	8·00	8·00	8·00	8·00	8·00	8·00	8·00
Ti ...	—	0·03	—	—	—	—	—	—	—	—	—	—	—	—
Fe‴ ...	1·57	1·30	1·41	1·41	1·56	1·51	1·33	1·27	1·37	1·50	1·32	1·36	1·50	1·12
Fe″ ...	2·21	3·27	2·85	2·96	2·97	2·77	2·92	2·78	2·83	2·68	3·03	2·54	2·67	3·49
Li ...	1·31	0·34	0·27	0·33	0·29	0·42	0·32	0·61	0·62	0·73	0·43	1·10	0·41	n.d.
Mn ...	0·08	—	0·13	0·07	0·08	0·06	0·05	0·07	0·05	0·04	0·05	0·06	0·05	0·08
Mg ...	0·01	0·01	—	0·11	0·02	0·01	0·04	0·10	0·01	0·07	0·01	—		0·08
Zn ...	0·10	0·05	0·04	0·06	0·07	0·06	0·07	0·07	0·07	0·07	0·05	0·05	0·09	0·03
Na ...	—	—	—	—	—	—	0·16	0·09	—	—	0·11	—	0·08	—
Y ...	5·28	5·00	4·70	4·94	4·99	4·83	4·89	4·99	4·95	4·99	5·00	5·14	4·80	4·80
Ca ...	0·03	0·15	0·49	0·38	0·30	0·30	0·15	0·33	0·17	0·11	0·15	0·05	0·08	0·69
Na ...	2·64	2·29	2·05	1·94	2·13	2·22	2·51	2·33	2·46	2·31	2·61	2·84	2·54	1·79
K ...	0·44	0·20	0·37	0·23	0·24	0·32	0·34	0·34	0·36	0·39	0·32	0·33	0·38	0·24
Mn ...	—	0·08	—	—	—	—	—	—	—	—	—	—	—	—
Fe″ ...	—	0·10	—	—	—	—	—	—	—	—	—	—	—	—
X ...	3·11	2·82	2·91	2·55	2·67	2·84	3·00	3·00	2·99	2·81	3·08	3·22	3·00	2·72
OH ...	0·41	1·38	1·49	1·78	1·70	1·47	1·15	1·16	1·36	1·35	1·05	1·14	1·35	1·65
F ...	1·62	0·52	0·70	0·65	0·70	0·80	1·09	1·16	1·02	1·07	1·10	1·22	0·98	0·28
Cl ...	0·05	0·03	0·02	0·01	0·02	0·01	0·02	0·01	0·03	0·04	—	0·02	0·01	0·10
OH,F,Cl	2·08	1·93	2·21	2·44	2·42	2·28	2·26	2·33	2·41	2·46	2·15	2·38	2·34	2·03
* Fe″/R	0·58	0·88	0·86	0·83	0·86	0·83	0·85	0·76	0·79	0·74	0·84	0·67	0·82	0·95
Fe″/Fe‴	1·36	2·59	1·88	1·95	1·81	1·78	2·15	1·89	1·90	1·75	2·13	1·68	1·71	3·12

* $R = Fe″+Mn+Mg+Li+Zn+Na.$

most of the excess alkali appears to have occupied vacant sites in order to make up for the electron deficiency caused by the decrease in Ca, there is also a slight correlation between increase of alkalis and substitution of Li for Fe″ in the Y-group. Throughout the series of alkali amphiboles Ca decreases from 0·69 atoms in A.16 to 0·03 in A.1 and alkalis increase from 2·03 atoms in A.1 to 3·17 in A.14.

The (OH)-group. In the Nigerian amphiboles both F and Cl are important substitutes for the hydroxyl ion. Chlorine is present in small amount (it is concentrated more in the hastingsites) and reaches 0·10

atoms in A.16, but F is more abundant and reference to table III shows that there is a general trend toward enrichment in F relative to (OH), the amount of fluorine varying from 0·28 atoms in A.16 to 1·62 atoms in A.1. There is a slight excess over the theoretical number of 2 atoms in the (OH)-group in a number of these minerals, and this may be due to errors in the determination of H_2O^+, particularly as the method used never gives very satisfactory results when used for amphiboles.
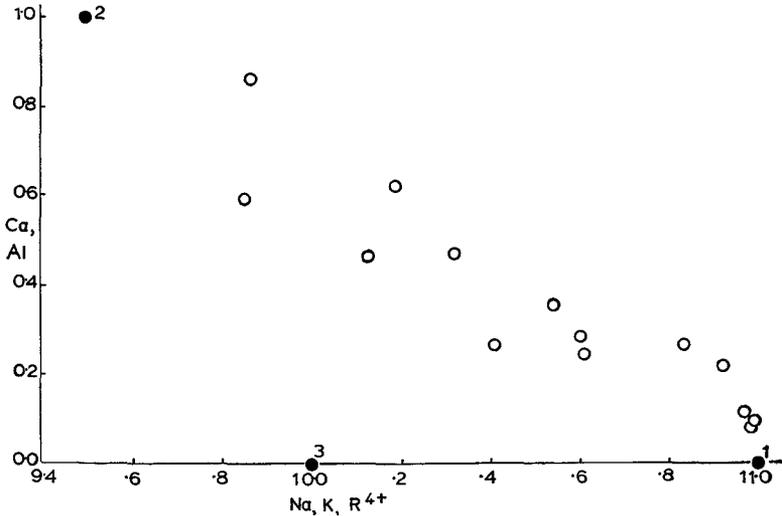
FIG. 3. Atomic variations in Ca+Al with Na+K+R^{4+} (where R^{4+} = Si, Ti, and Zr). Open circles represent Nigerian alkali amphiboles. Closed circles: 1 is end-member arfvedsonite (after Sundius); 2 is natural arfvedsonite (after Miyashiro), and 3 is end-member riebeckite.

General considerations. The major substitutions in the alkali amphiboles studied are those of Ca for alkali and, to a lesser extent, Si for Al. It should, therefore, be possible to show regular variation of $Ca''Al'''$ with $(Na, K)R^{iv}$ (where R^{iv} is any quadrivalent ion). Fig. 3 shows that there is a close correlation between the variations, the group of minerals varying fairly regularly, and approximately between the 'extremes' of arfvedsonite composition as represented by the Miyashiro and Sundius formulae. It is obvious from fig. 3 that arfvedsonites with formulae close to those of both Miyashiro and Sundius can be found in alkali granites, and it is also obvious that none of the amphiboles analysed approaches the formula of the theoretical riebeckite, which has been plotted on the same figure. The Fe''/Fe''' ratios in the analysed

amphiboles are much more variable than those allowed for in the formulae of Miyashiro or Sundius, but this is not an uncommon feature of natural arfvedsonites and riebeckites. In view of the fact that all the Nigerian alkali amphiboles show partial or complete filling of the vacant lattice sites with alkalis, together with the fact that many of them contain appreciable amounts (atomic) of calcium, it would seem that using the classifications of Sundius and Miyashiro, the Nigerian minerals would be
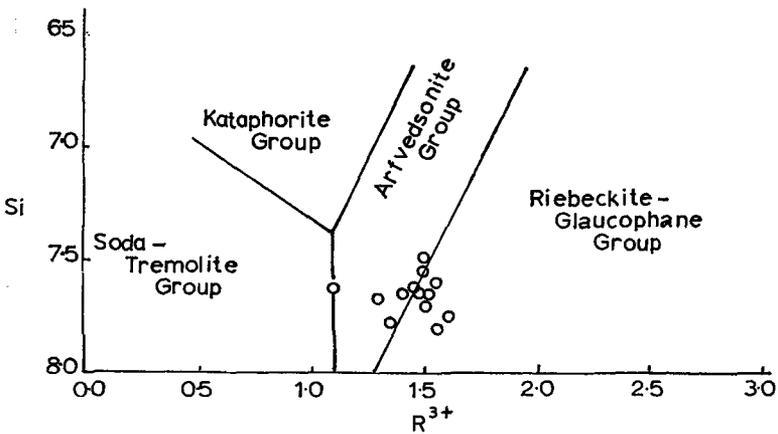
FIG. 4. (After Miyashiro.) Atomic variation in Si with R^{3+} (where R^{3+} = Al, Fe‴) in the alkali amphiboles. Open circles represent Nigerian alkali amphiboles.

more correctly described as arfvedsonites or riebeckitic arfvedsonites than as riebeckites.[1]

A large proportion of the other magmatic iron-rich alkali amphiboles that have been described as riebeckite are actually riebeckitic arfvedsonites in this sense and only a very few show a close approach to the theoretical formula for the end-member riebeckite, the closest approximations to the latter being the riebeckites described from Quincy, Massachusetts, by Palache and Warren (1911) and from the felsite dyke in Shetland, described by Phemister, Harvey, and Sabine (1950). Ernst (1962) has also pointed out that the analyses of the amphiboles from these two areas plot close to the theoretical composition of riebeckite.

The position of the Nigerian minerals in the Miyashiro classification can be seen in fig. 4.

[1] Ernst (1962) has suggested the name fluorarfvedsonite for a number of iron-rich alkali amphiboles from Nigeria.

Ferrohastingsites

X-group. Ca is always slightly lower in amount than the formula demands, and both Ca and alkalis show only very slight variations in atomic proportions.

TABLE IV. Chemical analyses, formulae, and optical properties of the ferrohastingsites. For key to these analyses, see p. 363.

	A.17.	A.18.	A.19.	A.20.			A.17.	A.18.	A.19.	A.20.
SiO_2	40·20	39·43	38·08	38·10	Si ⎫		6·51	6·43	6·33	6·34
Al_2O_3	8·32	8·65	7·67	8·97	Al ⎬ Z		1·49	1·57	1·50	1·66
TiO_2	2·06	2·20	2·23	1·95	Ti ⎭		—	—	0·17	—
Fe_2O_3	3·66	4·89	6·41	6·80	Total		8·00	8·00	8·00	8·00
FeO	25·52	25·59	28·81	27·50						
MnO	0·48	0·70	0·54	0·51	Al ⎫		0·10	0·10	—	0·10
MgO	4·05	2·43	1·09	0·78	Ti ⎬ Y		0·25	0·27	0·11	0·24
ZnO	0·09	0·14	n.d.	0·22	Fe''' ⎭		0·44	0·60	0·82	0·85
CaO	10·30	10·04	9·45	9·47	Total		0·79	0·97	0·93	1·19
Na_2O	2·12	2·29	1·85	2·18						
K_2O	1·33	1·61	1·52	1·69	Fe'' ⎫		3·44	3·50	4·01	3·82
P_2O_5	0·26	0·21	nil	0·13	Mn ⎬ Y		0·07	0·10	0·08	0·07
H_2O+	0·98	1·10	0·65	0·58	Mg ⎭		0·98	0·59	0·27	0·19
H_2O-	nil	0·01	nil	0·06	Total		4·49	4·19	4·36	4·08
F	0·48	0·29	0·58	0·58						
Cl	0·66	0·81	1·98	0·72	Ca ⎫		1·74	1·71	1·68	1·66
	100·51	100·39	100·86	100·24	Na ⎬ X		0·66	0·72	0·59	0·70
Less O					K ⎭		0·27	0·34	0·32	0·36
$= Cl, F$	0·35	0·31	0·69	0·41	Total		2·67	2·77	2·59	2·72
Total	100·16	100·08	100·17	99·83	OH		1·06	1·20	0·72	0·71
					F		0·24	0·15	0·30	0·30
					Cl		0·18	0·23	0·56	0·21
					Total		1·48	1·58	1·58	1·22

				A.17.	A.18.	A.19.	A.20.
α	...	...	...	1·687	1·702	1·705	1·704
β	...	...	...		?1·713		
γ	...	...	...	1·707	1·720	1·718	1·721
γ–α	...	...	...	0·020	0·018	0·013	0·017
Extinction γ ∧ [001]				16°±4°		10°	11°
α	...	...	...straw yellow	light straw	pale buff	?
β	...	...	...pale greenish-brown	deep straw	pale grey-green	dull grey-green
γ	...	...	...brownish-green	deep olive-green	grey-green	greyish green
Optical sign		...	—ve	—ve	—ve	—ve

Y-group. Fe''' should be equal to 1 atom in this group but the actual number of atoms present varies from 0·44 atoms in A.17 to a maximum of 0·85 in A.20. (See table IV.) Despite this variation there is very little change in the amount of substitution of Ti and Al for Fe''', the limits of substitution of these two elements (totalled together) being 0·11 atoms in A.19 and 0·37 atoms in A.18. Fe''' shows a slight increase with

decrease of Ca. Fe″ can have a maximum of 4 atoms in the Y-group in ferrohastingsites, but both Mn and Mg may be present as substitutes. The amount of Mn present is not significant but Mg decreases regularly as Fe″ increases, the Fe″/Mg ratio (molecular) ranging from 3·5 to 20. Fe″ and Fe‴ increase together in the minerals but Fe‴ increases more rapidly than Fe″ and the Fe″/Fe‴ ratio consequently decreases from approximately 8 in A.17 to 4·5 in A.20. The total number of atoms that can occupy Y-group sites varies from 5·16 in A.18 to 5·29 in A.19 and it is probable that Mn and a little Fe″ are occupying X-group sites.

Z-group. Table IV shows that there is a regular decrease of Si relative to Al in this group. Generally there is enough Al present to make up the theoretical number of 8 atoms for this group, except for A.19 where a small amount of Ti has had to be included with Al. There is a slight correlation between increase of Al and decrease of Ca (in the Y-group).

(OH)-group: Chlorine is more abundant (particularly in A.19 where the amphibole appears to have been slightly altered) in these ferro-hastingsites than in the alkali amphiboles, but fluorine is less so. There is a slight deficiency in the (OH) group in all the hastingsites, the maximum number of ions present being 1·58 in A.19, compared with a theoretical limit of two.

Until more analyses of calc-alkali amphiboles from Nigeria have been carried out, no satisfactory discussion of their chemical variations can be entered into and any trends shown to exist may be purely fortuitous. However, the change in the Fe″/Mg ratio may indicate an important trend towards iron enrichment in these amphiboles. It will also be necessary to await further analyses of calc-alkali amphiboles before deciding whether any solid solution exists between the latter group and the alkali amphiboles.

Optical methods and optical properties. Refractive indices were determined by the immersion method, employing sodium light, and using a refractometer to check the indices of the oils. All refractive index measurements were made in duplicate on different occasions. For the alkali amphiboles the indices determined are probably very close to α and γ. The strong absorption, high dispersion, and very small size of grains that must be used make any optical work on alkali amphiboles extremely difficult, and the accuracy of the refractive indices obtained is not thought to be better than $\pm 0·003$. The sign of elongation of these minerals was always found to be negative but the optical sign was not determined. Determination of $2V$ was generally impossible on the alkali amphiboles, but where any attempt could be made to measure the angle

it was between 70° and 80°. It was measured directly on a Leitz 4-axis universal stage, measurements being made on a number of grains and results averaged. Optical properties of the amphiboles are shown in tables II and IV.

Close correlation of optical properties with chemical composition of the alkali amphiboles is not possible due mainly to the uncertain accuracy of refractive index measurements, but some general comments can be made. Of the more common major constituents of the minerals, the alkalis, ferrous and ferric iron, and calcium all affect the refractive indices to some degree. Ca and the alkalis (which replace Ca in the X-group) have opposite effects on α' and γ', the indices showing a general decrease with decreasing Ca and increasing alkalis; in the Y-group, increases of Fe″ and Fe‴ cause an increase in the refractive indices, although increases in both can be correlated more closely with increases in γ' than α'. Obviously the lack of very close correlation between increases of the elements mentioned and increases in α' and γ' can be partly explained by the presence in the lattice of other less common constituents, more particularly by the presence of F and Li (both present in significant amount). Increases in F or Li cause a general decrease in α' and γ' but an increase of either of these elements can be correlated more closely with a decrease in α' than in γ'. It is obvious, therefore, that although the higher refractive indices belong to the more iron-rich members of the alkali amphiboles, the complexity of possible substitutions in their structure, and the marked effect that the presence of large amounts of F or Li has on refractive indices, mean that only a general idea of composition of these minerals can be obtained by means of optical measurements.

Optical data for the ferrohastingsites are given in table IV. Generally they have smaller $2V$, larger extinction angle, higher refractive indices, and greater birefringence than the alkali amphiboles, and do not show such intense absorption as the latter.

Mention has been made, in the section on petrography, of the fact that the alkali amphiboles do not always show extinction in ordinary light in sections parallel to (010); this phenomenon is common in these amphiboles and has been discussed by Eskola and Sahlstein (1930), Yagi (1953), Sahama (1956), and Shoda (1957). Eskola and Sahlstein and Sahama concluded, after optical and X-ray work, that arfvedsonite consisted of an intergrowth of two amphiboles, but Shoda (1957) examined arfvedsonite from Kansenri, Korea, and concluded that the apparent anomalies are merely elliptical polarization due to strong

absorption in the mineral. X-ray work, carried out by M. Frost of Manchester University on single crystals from several of the amphiboles discussed in this paper, does not indicate any intergrowth of two amphiboles.

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