

Some observations on igneous ferrohastingsites

By G. BORLEY, Ph.D., B.Sc., A.R.C.S.,
Department of Geology, Imperial College,

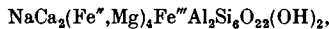
and

M. T. FROST, B.Sc.,
Department of Geology, Manchester University

[Read 27 September 1962]

Summary. Nine ferrohastingsites from the Younger Granites of Northern Nigeria and five from the nepheline-bearing rocks in the Marangudzi complex of Southern Rhodesia have been analysed chemically and their optical properties and unit-cell parameters determined.

All the minerals have compositions that can be expressed by the formula



but the Nigerian minerals differ from those of Marangudzi in their lower alumina contents, generally greater degree of iron enrichment, lower potassium, and more variable fluorine contents. These differences are considered to reflect the differences in composition of their respective parent rocks. The compositional similarities between some hastingsites and barkevikite are commented upon and the pleochroism of barkevikite is briefly discussed.

Refractive indices of the analysed hastingsites have been plotted on the optical curves of Tröger. It is suggested that such curves are of limited use and that variations in unit-cell parameters might be a more useful method of determining the iron contents of hastingsites.

The variation in cell parameters with variation in chemical composition of the analysed minerals is also discussed.

IN a previous paper the authors discussed a number of alkali amphiboles from the Younger Granites of Nigeria, and a brief mention was also made of four hastingsites from the same granites. Chemical, optical, and unit-cell data are now available for four more hastingsites from the Younger Granites and also for an amphibole that is intermediate in all its properties between the hastingsites and the alkali amphiboles mentioned above. Analyses of five hastingsites from rocks occurring in the Marangudzi Ring Complex of Southern Rhodesia have also been made available to the authors, and the data for these minerals are compared with the data for the Nigerian hastingsites.

The first section of this paper was written by the first author and the second section, on unit-cell data, by the second author.

Key to tables I, II, III, IV, and V

- R.17. PB 38 Mbul hornblende-fayalite granite. Kaleri Complex, Jos Plateau, Nigeria.
 A.17. Hastingsite from R. 17.
 R.18. PB 48 Syenite from Pankshin Complex. Jos Plateau, Nigeria.
 A.18. Hastingsite from R.18.
 R.19. PB.96 Early hornblende-biotite granite. Jos-Bukuru complex, Jos Plateau, Nigeria.
 A.19. Hastingsite from R.19.
 R.20. PB 97 Early hornblende-biotite granite. Jos-Bukuru complex, Jos Plateau, Nigeria.
 A.20. Hastingsite from R.20
 R.21. PB.47 Hornblende-fayalite granite. Pankshin Complex, Jos Plateau, Nigeria.
 A.21. Hastingsite from R.21
 R.22. PB 45 Hornblende-biotite granite. Pankshin Complex, Jos Plateau, Nigeria.
 A.22. Hastingsite from R.22
 R.23. PB.51 Hornblende-biotite granite. Pankshin Complex, Jos Plateau, Nigeria.
 A.23. Hastingsite from R.23
 R.24. PB.71 Hornblende-fayalite porphyry. Shere Hills, Jos Plateau, Nigeria.
 A.24. Hastingsite from R.24
 R.25. PB.13 Quartz-fayalite porphyry. Liruei Complex, Jos Plateau, Nigeria.
 A.25. Amphibole from R.25.
 R.26. A.2 Foyaite from Marangudzi complex, S. Rhodesia.
 A.26. Hastingsite from R.26
 R.27. A.20. Foyaite from Marangudzi complex, S. Rhodesia.
 A.27. Hastingsite from R.27
 R.28. A.15 Foyaite from Marangudzi complex, S. Rhodesia.
 A.28. Hastingsite from R.28
 R.29. G.141 Syenite from Marangudzi complex, S. Rhodesia.
 A.29. Hastingsite from R.29
 R.30. G.76A Foyaite from pulaskite ring, Marangudzi complex.
 A.30. Hastingsite from R.30.
- | | |
|---|-----------------------------------|
| 1. Barkevikite from sodalite syenite, Square Butte, Montana | } From J. F. G. Wilkinson (1961). |
| 2. Barkevikite from nepheline syenite, Skuttersundskjar | |
| 3. Barkevikite from nepheline syenite, Stavarnsjo | |
| 4. Barkevikite from foyaite, S. Vincente, Cape Verde | |
| 5. Kaersutite from Alno | } From R. A. Howie (1963). |
| 6. Kaersutite from Lugar | |
| 7. Barkevikite from essexite, Fuerteventura, Canary Isles. | From J. F. G. Wilkinson (1961). |

Occurrence of the hastingsites. The location and petrography of the granites from which four of the Nigerian hastingsites have been separated have already been described by Borley (1963), the granites being referred to as R.17 to R.20 and the minerals A.17 to A.20 inclusive. Of the remainder of the Nigerian granites, R.21 is an amphibole-fayalite granite and R.22 and R.23 are hornblende-biotite granites from Pankshin

complex, R.24 is an amphibole-fayalite porphyry from Shere Hills, and R.25 is a quartz-fayalite porphyry from Liruei. Modal analyses of the rocks are given in Table I.

R.21 is a fine to medium-grained granite containing some coarse perthite grains; the amphibole has α fawn and γ deep brownish-green and occurs as grains that are ragged and interstitial or lath-shaped.

TABLE I. Modal analyses of some parent rocks of the analysed hastingsites. Modal analyses of Nigerian granites R.17 to R.20 inclusive have been given already by Borley (1963)

| | R.21 | R.22 | R.23 | R.24 | R.25* | R.26 | R.29 |
|---------------------------------|------|------|------|------|-------|------|------|
| Quartz | 27.3 | 27.8 | 33.5 | 25.7 | 21.8 | — | 6.8 |
| Perthite | 56.6 | 49.8 | 57.7 | 63.6 | 62.3 | 59.2 | 76.4 |
| Plagioclase (mainly albite) ... | 11.9 | 16.2 | 2.0 | 1.4 | — | 5.9 | 5.3 |
| Amphibole | 2.6 | 2.4 | 3.1 | 5.1 | 6.2 | 17.1 | 11.1 |
| Biotite | tr. | 3.3 | 2.0 | 0.3 | — | — | — |
| Pyroxene | tr. | — | — | — | 5.9 | 4.7 | — |
| Fayalite | 0.8 | — | — | 2.8 | 3.3 | — | — |
| Nepheline | — | — | — | — | — | 7.3 | — |
| Sodalite | — | — | — | — | — | 2.1 | — |
| Opaque minerals | 0.2 | 0.2 | 1.4 | 0.7 | 0.5 | — | 0.3 |
| Zircon | tr. | tr. | — | tr. | — | — | — |
| Fluorite | 0.5 | tr. | — | 0.4 | — | — | — |
| Allanite | tr. | tr. | — | — | — | — | — |
| Others | — | — | — | — | — | — | — |
| Groundmass: phenocrysts ... | — | — | — | — | 52:48 | — | — |

* Phenocrysts only, groundmass too fine-grained for counting.

R.22 and R.23 from Pankshin have a number of similarities but the amphibole in R.22 is generally found as subhedral grains with α light fawn and γ olive-green. Although there is some variation in grain size in R.24 most of the sections examined are non-porphyritic; amphibole with α fawn and γ dull greenish-brown is sparsely developed and is subordinate, modally, to fayalite. The other porphyry, R.25, has a very different texture from R.24 and contains abundant phenocrysts of high-temperature quartz, perthite, hedenbergitic pyroxene, and fayalite, in a very fine-grained groundmass; most of the amphibole in this rock occurs either as rims on fayalite, or as completely sieved grains (which might be porphyroblasts) in the groundmass; the amphibole is slightly variable in colour, some of the smaller crystals in the groundmass being blue or bluish green, but usually has α pale straw and γ bluish yellow-green.

The Marangudzi ring complex is located near the southern border of Southern Rhodesia, between longitudes 30° and 31° E. and on latitude

22° S. It is intrusive into rocks of the basement complex, and the members of the ring complex itself cover a total area of approximately 33 square miles. The complex consists of two groups of ring intrusions, a larger 'outer' group made up of granite and quartz-syenites, and a smaller eccentrically placed 'inner' group formed of later intrusions of foyaites, pulaskite, and juvite. Between these two groups of granitic and alkaline rocks lies an older and extensive body of olivine-gabbro and in addition a second mass of gabbro is found outside the south-eastern part of the outermost granite intrusion. A complete geological account of the complex has been given by Gifford (1960) and Rees (1960).

Hastingsites have been separated by Gifford and Rees from five of the intrusions occurring in the Marangudzi Complex, and all but one of these minerals have come from nepheline-bearing rocks.

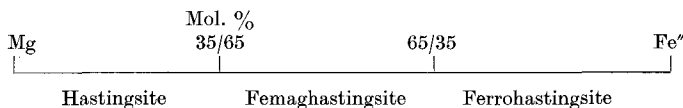
R.29 is a quartz-syenite of medium grain size and is rich in perthitic alkali feldspar; the amphibole has α pale pinky-yellow and γ deep olive-green and the grains, which rarely exceed 1.5 mm in length, are ragged and sometimes interstitial. R.28 is a syenite containing abundant nepheline and perthite, together with an amphibole with α light straw and γ deep bluish-green, which forms subhedral grains approximately 1 mm in length; lath-shaped crystals of amphibole are frequently twinned and the mineral is slightly zoned. R.26, R.27, and R.30 are foyaites, R.30 being found within the pulaskite ring intrusion. In R.26 the amphibole, α light straw and γ deep green, occurs as grains that are either tabular in shape and 1.5 mm to 2 mm in size, or lath shaped and up to 6 mm in length. R.27 is rich in an amphibole that is often zoned and has α buff and γ brownish green; the larger amphibole grains, which are about 3 mm in size, appear to be of early crystallization but many of the smaller grains are interstitial and of late formation. R.30, the foyaite from the pulaskite ring, contains an amphibole with α light brown and γ dull dark green that is associated with, or often encloses, a pale green pyroxene. Modal analyses of R.26 and R.29 are given in table I.

Apart from their contrasted mineralogy the Marangudzi rocks differ from the Nigerian granites in containing a much greater proportion of ferromagnesian minerals and in showing less textural variation, secondary alteration, and replacement.

The hastingsite group. The first attempt to subdivide the hastingsite group was made by Billings (1928) on the basis of the ratio Fe''/Mg (molecular proportions), the three subdivisions being: ferrohastingsite

with $Fe''/Mg > 2$, femaghastingsite with $Fe''/Mg > 0.5 < 2.0$, and magnesiohastingsite with $Fe''/Mg < 0.5$. Sundius (1946), in his classification of the calciferous amphiboles, drew attention to the similarity that existed between many of the magnesium-rich hastingsites of Billings and pargasite, $NaCa_2Mg_4AlAl_2Si_6O_{22}(OH)_2$, and he also suggested the formula $NaCa_2Mg_4Fe''Al_2Si_6O_{22}(OH)_2$ for hastingsite. In general the compositions of the calcium-alkali-rich amphiboles are limited by those of four end-members: pargasite; ferropargasite, $NaCa_2Fe''_4AlAl_2Si_6O_{22}(OH)_2$; hastingsite, which is related to pargasite by the substitution of Fe''' for Al; and ferrohastingsite, $NaCa_2Fe''_4Fe'''Al_2Si_6O_{22}(OH)_2$, which is related to ferropargasite by a similar substitution.

For the purpose of this present discussion the author has subdivided the hastingsite group in the following manner:



Preparation of material and analytical methods. Details of the preparation of material and analytical methods have been given by Borley (1963), the only change being in the method of determining silica, for which the combined gravimetric-colorimetric method recommended by Jeffery and Wilson (1960) was used.

Variations within the hastingsites. Chemical analyses and optical properties of the two groups of hastingsites are given in table II and their formulae are given in table III. The formulae of the Marangudzi hastingsites have been calculated on the basis of 24 (O + OH + F) in the usual way, but the formulae of the minerals from the Nigerian granites have been calculated on the basis of 23 oxygen atoms as it was not possible to determine H_2O+ because of insufficient material.

Reference to fig. 1 shows that the Nigerian hastingsites are slightly deficient in alumina content and the amount of Al in tetrahedral coordination reaches a maximum of 1.732 atoms in A.20, compared with a theoretical number of 2.0 atoms. A slight excess of Si partially compensates for this deficiency in Al, nevertheless a small amount of Ti has had to be included in the Z-group in order to bring the total up to 8 atoms. In contrast four of the Marangudzi minerals have a slight excess of Al above that required for the Z-group, in which Al has a maximum value of 2.106 atoms in A.27. Perhaps the best-known group of genetically

TABLE II. Analyses and optical properties of hastingsites. Key on p. 647. Analyses 17 to 25 by Dr. G. Borley, 26 to 30 by Dr. I. S. E. Carmichael

| | A.17 | A.18 | A.19 | A.20 | A.21 | A.22 | A.23 | A.24 | A.25 | A.26 | A.27 | A.28 | A.29 | A.30 |
|--------------------------------|--------|--------|--------|--------|-------|--------|-------|-------|--------|----------|--------|----------|----------|--------|
| SiO ₃ | 40.20 | 39.43 | 38.08 | 38.10 | 41.70 | 39.10 | 40.98 | 39.32 | 46.57 | 37.34 | 36.73 | 36.80 | 37.08 | 37.48 |
| Al ₂ O ₃ | 8.32 | 8.65 | 7.67 | 8.97 | 4.61 | 8.47 | 8.63 | 9.39 | 1.89 | 10.92 | 12.08 | 10.15 | 11.77 | 11.74 |
| TiO ₃ | 2.06 | 2.20 | 2.23 | 1.95 | 1.89 | 2.22 | 1.92 | 1.92 | 1.43 | 1.12 | 1.56 | 0.96 | 0.89 | 2.63 |
| Fe ₂ O ₃ | 3.66 | 4.89 | 6.41 | 6.80 | 4.29 | 6.01 | 4.36 | 7.91 | 3.73 | 7.08 | 5.69 | 7.58 | 5.82 | 5.21 |
| FeO | 25.52 | 25.59 | 28.21 | 27.50 | 28.32 | 26.61 | 22.31 | 21.93 | 31.38 | 20.40 | 21.43 | 23.74 | 22.02 | 19.16 |
| MnO | 0.48 | 0.70 | 0.54 | 0.51 | 0.65 | 0.64 | 0.62 | 0.32 | 0.68 | 0.94 | 0.90 | 1.57 | 1.33 | 0.78 |
| MgO | 4.05 | 2.43 | 1.09 | 0.78 | 2.08 | 1.97 | 5.63 | 1.46 | 0.30 | 4.30 | 3.73 | 1.95 | 3.46 | 5.58 |
| ZnO | 0.09 | 0.14 | n.d. | 0.22 | 0.17 | 0.12 | n.d. | n.d. | n.d. | 0.05 | 0.05 | 0.06 | 0.04 | 0.06 |
| CaO | 10.30 | 10.04 | 9.45 | 9.47 | 10.31 | 10.21 | 10.97 | 11.00 | 5.90 | 10.90 | 10.78 | 10.22 | 10.94 | 11.27 |
| Na ₂ O | 2.12 | 2.29 | 1.85 | 2.18 | 2.10 | 2.17 | 1.97 | 2.24 | 4.54 | 2.87 | 2.68 | 2.94 | 2.54 | 2.25 |
| K ₂ O | 1.33 | 1.61 | 1.52 | 1.69 | 1.42 | 1.48 | 1.22 | 1.42 | 1.18 | 2.00 | 2.46 | 1.88 | 2.07 | 2.15 |
| P ₂ O ₅ | 0.26 | 0.21 | nil | 0.13 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| H ₂ O ⁺ | 0.98 | 1.1 | 0.65 | 0.58 | n.d. | n.d. | n.d. | n.d. | n.d. | 1.03 | 1.06 | 0.98 | 0.87 | 0.82 |
| H ₂ O ⁻ | nil | 0.01 | nil | 0.06 | 0.14 | 0.07 | 0.41 | nil | 0.13 | 0.02 | 0.05 | 0.05 | 0.05 | 0.04 |
| F | 0.48 | 0.24 | 0.58 | 0.58 | 1.85 | 1.13 | 1.12 | 3.02 | 3.84 | 1.51 | 1.57 | 2.06 | 1.94 | 1.84 |
| Cl | 0.66 | 0.81 | 1.98 | 0.72 | n.d. | n.d. | n.d. | n.d. | n.d. | 0.10 | 0.08 | 0.05 | 0.14 | 0.16 |
| <i>Less O_i for</i> | 100.51 | 100.34 | 100.86 | 100.24 | 99.53 | 100.20 | 99.97 | 99.93 | 101.57 | 100.58 | 100.85 | 100.99 | 100.96 | 101.17 |
| F, Cl ... | 0.35 | 0.28 | 0.69 | 0.41 | 0.78 | 0.47 | 0.47 | 1.27 | 1.62 | 0.66 | 0.68 | 0.88 | 0.85 | 0.81 |
| | 100.16 | 100.06 | 100.17 | 99.83 | 98.75 | 99.73 | 99.50 | 98.66 | 99.95 | 99.92 | 100.17 | 100.11 | 100.11 | 100.36 |
| α' | 1.687 | 1.702 | 1.705 | 1.704 | 1.703 | 1.701 | 1.699 | 1.695 | 1.693 | 1.701 | 1.692 | 1.709-10 | 1.700 | 1.696 |
| γ' | 1.707 | 1.720 | 1.718 | 1.721 | 1.725 | 1.718 | 1.712 | 1.711 | 1.701 | 1.715-16 | 1.711 | 1.721-2 | 1.711-12 | 1.711 |
| γ'-α' | 0.020 | 0.018 | 0.013 | 0.017 | 0.022 | 0.017 | 0.013 | 0.016 | 0.008 | 0.014-15 | 0.019 | 0.011-12 | 0.011-12 | 0.015 |

related ferrohastingsites are those occurring in granites and granite-gneisses of the Adirondacks region, New York, described by Buddington and Leonard (1953); for comparative purposes the Si and Al contents of these minerals have been plotted on fig. 1, their position being intermediate between those from Nigeria and Marangudzi.

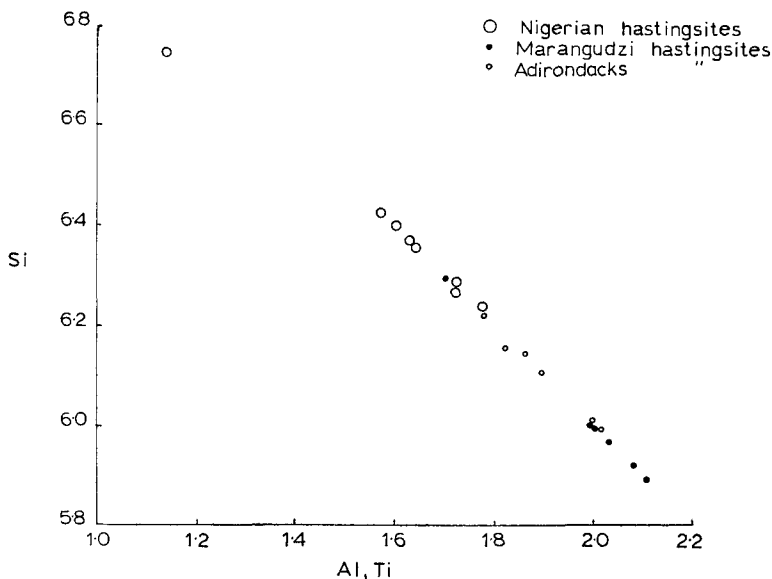


FIG. 1. Atomic variation in Si with Al+Ti in analysed ferrohastingsites.

Of the cations that may occupy structural sites in the *Y*-group, Al is generally absent and Fe^{III} is low in the Nigerian minerals, and these deficiencies are only partly offset by the presence of Ti in octahedral coordination. Apart from A.28, however, the Marangudzi hastingsites all contain Al in the *Y*-group together with Ti and Fe^{III} and the three, totalled together, are slightly in excess of the theoretical requirement. The Nigerian hastingsites are rich in Fe^{II} and a high degree of iron enrichment in these minerals is indicated by the large increase in the ratio $(Fe^{II} + Mn) \times 100 : (Fe^{II} + Mn + Mg)$ (see table III). A similar enrichment in iron occurs in the Marangudzi hastingsites and it is of interest to note that the amphibole present in the early intruded granite (A.29) is slightly more enriched in iron than the amphiboles from some of the later intruded foyaites. Accompanying the increase in Fe^{II} in the Nigerian

hastingsites is a considerable increase in Fe^{III} relative to Fe^{II} , shown by a marked decrease in the Fe^{II}/Fe^{III} ratio, which is in contrast to the Marangudzi hastingsites, which show only slight changes in the Fe^{II}/Fe^{III} ratio. One minor constituent of interest is zinc although it is unimportant atomically. In the alkali amphiboles from the Nigerian granites

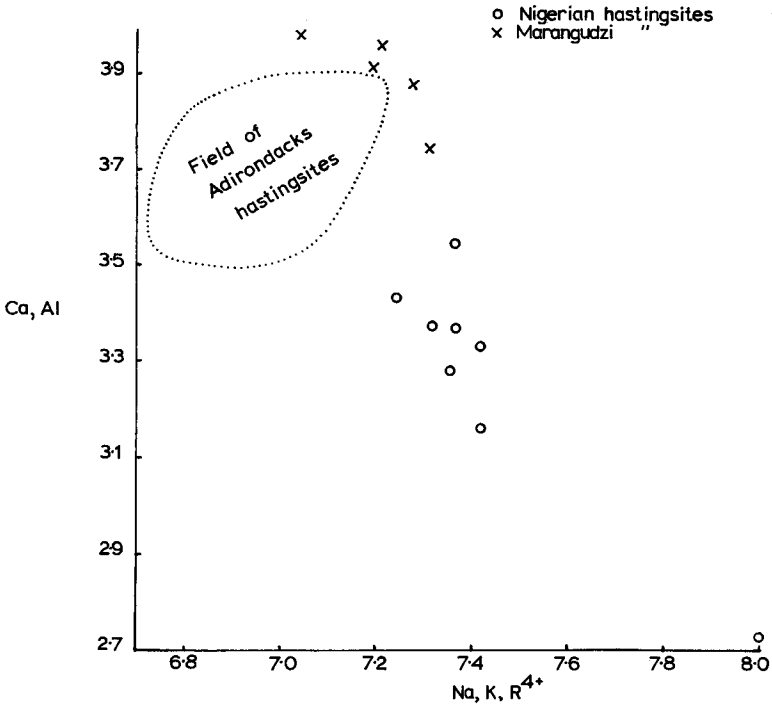


FIG. 2. Atomic increase in $Si + Na + K$ with decrease in $Ca + Al$ in ferrohastingsites.

(Borley, 1963) the ZnO content had a range from 0.3 % to 0.9 % but reference to table II will show that the hastingsites have a maximum ZnO content of 0.22 % in A.20, and this low percentage undoubtedly reflects the low zinc content of the parent rocks of these minerals.

None of the analysed hastingsites contains quite as much calcium as the formula allows and there is also a slight deficiency in total alkalis in several of the Nigerian minerals, whereas there is a slight excess of total alkalis in the Marangudzi minerals, which have a high potash content. Fig. 2 shows the variation in $Ca + Al$ with $Na, K,$ and Si in the

hastingsites and the field within which the Adirondacks hastingsites occur is also indicated.

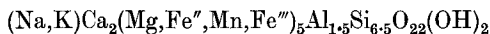
No real comparison can be made of the relative amounts of (OH) and volatiles present in the hastingsites, but both F and Cl show more variation in the Nigerian minerals than in those from Marangudzi. Where it has been determined the amount of Cl present in the Nigerian hastingsites is high with a maximum value of 1.98 % in A.19, which is a slightly altered mineral, and the only comparable hastingsites are those from the Adirondacks, which have an average chlorine content of 0.50 %.

In general the composition of the hastingsites from the Nigerian granites is closely related to the composition of the granites themselves, which are low in alumina, high in silica and total iron (relative to magnesia), and which are only slightly alkaline. Very little is known at the moment of the chemistry of the Marangudzi rocks, but their strongly undersaturated nature is indicated by a considerable development of feldspathoids (nepheline, leucite, and sodalite) and appears to be reflected in the composition of the hastingsites.

So far the composition of the amphibole A.25 has not been discussed and some comment on it is necessary. A number of amphiboles have been reported in the past that cannot be placed either in the hastingsite group or in any of the alkali amphibole sub-groups (Billings, 1928). Similarly A.25 cannot be allotted to a particular amphibole group although the low CaO, moderate alkali, and high total iron content make it slightly closer in composition to the alkali amphiboles than to the hastingsites from the Nigerian granites. Optically it also resembles the alkali amphiboles, having a strongly bluish tint to its colour and having lower refractive indices than the hastingsites. Its unit-cell parameters are also intermediate between the two types of amphibole as can be seen from fig. 5. Considering all these factors the author suggests that this amphibole provides reasonable evidence of limited solid solution between the hastingsites and alkali amphiboles from the Nigerian granites.

One point of interest that can be mentioned here is the close similarity in chemical composition that exists between some hastingsites and the brown or yellowish-brown amphibole, barkevikite, found in many syenites and undersaturated rocks. Billings (1928) apparently distinguished barkevikite from members of the hastingsite group but did not denote brown hastingsites or alkali-hastingsites by any special names, and Tröger (1956) used the name barkevikite for hastingsites with molecular percentages of Fe²⁺/Fe³⁺ between 50 % and 75 %. Wilkinson (1961) has pointed out that the composition of barkevikite is related

to that of end-member ferropargasite, and Deer, Howie, and Zussman (1963) have proposed the formula



for barkevikite. This formula suggests an alumina content that is slightly too low for many barkevikites and it could also embrace many other members of the hastingsite-ferrohastingsite series.

TABLE IV. Formulae of the barkevikites calculated on the basis of 24 (O+OH+F); some of these amphiboles would be classed as kaersutite by Wilkinson (1961).

Key on p. 647.

| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|--|-----|-------|--------------|-------------|-------|--------------|---------|-------|
| Si | ... | 6.14 | 6.29 | 6.35 | 5.97 | 5.696 | 5.728 | 5.60 |
| Al ^{iv} | ... | 1.86 | 1.71 | 1.65 | 2.03 | 2.304 | 2.272 | 2.28 |
| Ti ^{iv} | ... | — | — | — | — | — | — | 0.12 |
| Total Z | ... | 8.00 | 8.00 | 8.00 | 8.00 | 8.000 | 8.000 | 8.00 |
| Al ^{vi} | ... | 1.23 | 0.47 | 0.36 | 0.21 | 0.214 | 0.406 | — |
| Ti ^{vi} | ... | 0.15 | 0.03 | 0.05 | 0.14 | 0.325 | 0.632 | 0.44 |
| Fe ⁱⁱⁱ | ... | 0.45 | 0.88 | 0.77 | 1.37 | 0.529 | 0.140 | 1.12 |
| Fe ⁱⁱ | ... | 2.91 | 2.25 | 2.34 | 2.17 | 0.748 | 1.416 | 1.35 |
| Mn | ... | 0.02 | 0.17 | 0.13 | 0.10 | 0.006 | 0.020 | 0.04 |
| Mg | ... | 0.60 | 1.37 | 1.43 | 0.95 | 3.119 | 2.116 | 2.10 |
| Total Y | ... | 5.36 | 5.17 | 5.18 | 4.94 | 4.941 | 4.730 | 5.05 |
| Ca | ... | 1.80 | 1.73 | 1.73 | 1.87 | 1.929 | 2.145 | 2.00 |
| Na | ... | 0.91 | 1.11 | 1.10 | 1.05 | 0.571 | 0.641 | 0.78 |
| K | ... | 0.40 | 0.15 | 0.19 | 0.14 | 0.386 | 0.221 | 0.28 |
| Total X | ... | 3.11 | 2.99 | 3.02 | 3.06 | 2.886 | 3.008 | 3.06 |
| OH | ... | 0.26 | 1.20 | 1.49 | 1.28 | 2.20 | 1.83 | 1.13 |
| $\frac{(\text{Fe} + \text{Mn}) \times 100}{\text{Fe} + \text{Mn} + \text{Mg}}$ | | 83 | 64 | 63 | 71 | 19 | 41 | 40 |
| Fe ⁱⁱ /Fe ⁱⁱⁱ | ... | 6.5 | 2.6 | 3.0 | 1.6 | 1.4 | 11.2 | 1.2 |
| Mol. % | | | | | | | | |
| Fe ⁱⁱ | ... | 83 | 62 | 62 | 69 | 19 | 40 | 39 |
| Mg | ... | 17 | 38 | 38 | 31 | 81 | 60 | 61 |
| α | ... | — | 1.691 | 1.687 | 1.694 | 1.670 | 1.685-6 | 1.687 |
| γ | ... | — | 1.707 | 1.701 | 1.710 | 1.685-6 | 1.713 | 1.708 |
| $\gamma - \alpha$ | ... | — | 0.016 | 0.014 | 0.016 | 0.015-6 | 0.028 | 0.021 |
| α | ... | ... | yellow-brown | — | — | brown | — | — |
| β | } | dark | dark | green-brown | brown | brown | brown | dark |
| γ | | brown | brown | brown | — | — | — | brown |
| | | | | | | Oxygen Atoms | | |
| | | — | — | — | — | 23.995 | 23.990 | 24.00 |

A comparison of the analyses and formulae of the Marangudzi hastingsites (tables II and III) with the barkevikite formulae in table IV shows that there are a number of similarities between these minerals, although

barkevikites nos. 5, 6, and 7 are more comparable with many femaghas-tingsites. The most distinctive features of the composition of the barkevikites are the high alumina and low water contents of the majority of them, and the low water content in particular may be of some significance, implying either formation under slightly anhydrous conditions or secondary release of hydrogen from the (OH)-group. Typically, barkevikites are found in the same types of undersaturated rock as green or blue-green hastingsite and they presumably form under essentially similar conditions of P_{O_2} and T . Undoubtedly one of the most interesting properties of barkevikites is their brown pleochroism and this cannot be simply related to any one aspect of their very variable chemistry. It was suggested by Hall (1941) that a high Ti content was responsible for the red-brown colour of some biotites, but that a high Ti content accompanied by high Mg resulted in brown biotites. Chinner (1960) also considered that the Ti content of some brown biotites was the main cause of their colour, with the ferric to ferrous iron ratio playing a minor part. However, although these explanations could also be applied satisfactorily to a number of barkevikites they could not explain the colour of those barkevikites that are deficient in TiO_2 . Other factors that may be important when considering the colour of these minerals are the secondary oxidation of ferrous iron to ferric, which might be accompanied by a colour change in the mineral, and the possibility that one or more of the cations occupies a different lattice site from that it normally occupies and that this affects the optical properties of the mineral (as Ti in tetrahedral coordination is known to affect the optical properties of pyroxenes). The author suggests that the colour could be the result of Ti, or in some cases Fe^{III} , occupying tetrahedral sites instead of Al, but this is a very tentative proposal, for the wide compositional range shown by barkevikites suggests that there may be no single explanation of their pleochroism.

Optical properties of the hastingsites. The refractive indices of the analysed hastingsites were determined by the immersion oil method and the results are given in table II. Accuracy of the determinations is approximately ± 0.002 .

The establishing of useful optical determinative curves for amphiboles is made difficult by the complexity of their compositions, but optical curves for many of the amphibole subgroups were produced by Tröger (1956) and these are in frequent use. In fig. 3 *a* and *b* respectively the sections of Tröger's curves for γ and α that covered iron-rich members of the hastingsite group have been reproduced. The refractive indices of

the analysed hastingsites have been plotted against their Mg and Fe²⁺ contents, together with a number of other igneous hastingsites and the barkevikites of Wilkinson and Howie. It is obvious that except for approximate work the curves are of limited value, and this is probably because of the influence that minor cations such as Ti and Mn can have

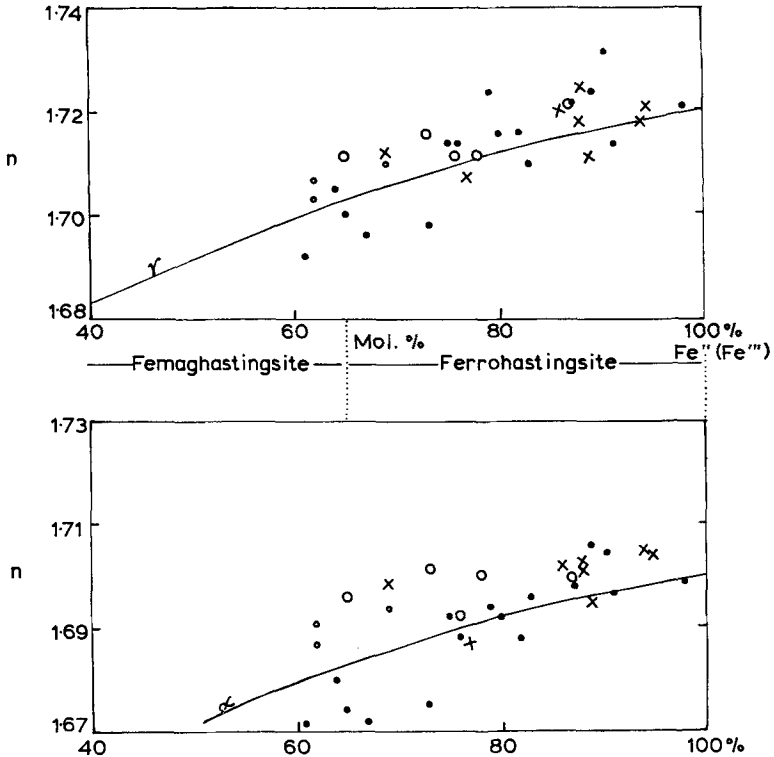


FIG. 3. *a* (top) and *b* (bottom). Refractive indices of hastingsites and barkevikites plotted against molecular percentages of Mg and Fe.
 X Nigerian hastingsites; O Marangudzi hastingsites; ● other hastingsites; ○ barkevikites.

on optical properties. The possible inaccuracy of data obtained from optical curves makes it necessary to find supplementary methods of estimating the composition of hastingsitic amphiboles, when chemical analysis is not feasible. In figs. 4 *a* and *b* respectively, the $(\text{Fe}^{2+} + \text{Mn}) \times 100 : (\text{Fe}^{2+} + \text{Mn} + \text{Mg})$ ratios and the total iron contents of the analysed hastingsites have been plotted against the length of the *b*-parameter. The correlation between total iron and length of *b* is

close enough to suggest that measurement of b might prove to be a rapid and an accurate way of determining the total iron content of many amphiboles. However, other ions such as Ca and Li also affect the length of b and it will be necessary to take this into account when assessing the value of using this parameter for determinative purposes.

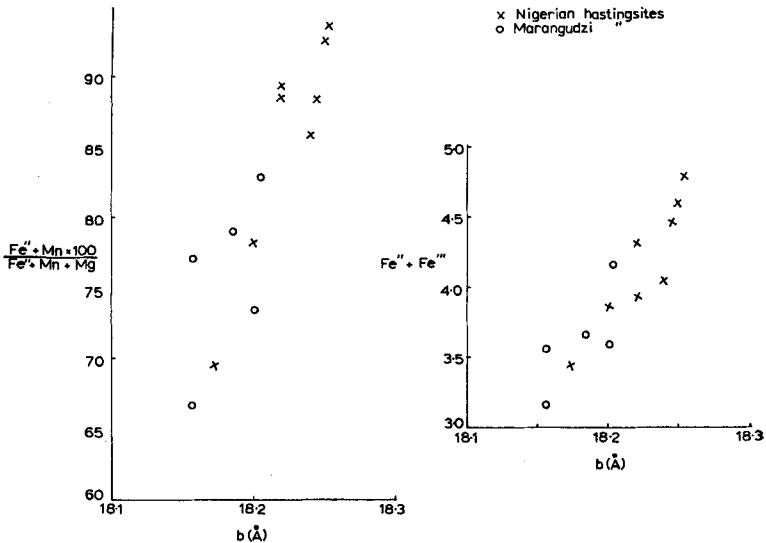


FIG. 4. *a* (left): Increase in length of b with increasing iron enrichment in analysed hastingsites. *b* (right): Increase in length of b with increase in total iron in analysed hastingsites.

X-ray data

Experimental methods and computations. Cell parameters were determined using a Philips X-ray diffractometer and filtered $\text{Co-K}\alpha$ radiation. Each specimen was ground in an agate mortar and, depending on the amount of specimen available, either packed into a glass cavity approximately 5×10 mm in dimension, or smeared onto a glass slide. Traces of A.21, A.22, A.23, A.24, and A.25 were produced from smears; the remainder from powder in cavities. Instrument settings were as follows: time constant 4; scanning $\frac{1}{4}^\circ/\text{min}$; chart speed 400 mm/h; divergence and scatter slits 1° . Chart measurements of 2θ were made up to about $50^\circ 2\theta$, in most cases on more than one trace. The measurements were made with a vernier rule and have a standard deviation of

0.005°. The distance measured was that from the estimated centre of each reflection (at 5/6 peak height) to the nearest degree mark.

A least squares method was adopted for the computation of the cell

TABLE V. Cell parameters (*C2/m* orientation)

| | <i>a</i> | <i>b</i> | <i>c</i> | β | <i>V</i> | <i>a sin β</i> |
|-----------|----------|----------|----------|----------|----------------------|---------------------------------|
| A.27 ... | 9.941 Å | 18.156 Å | 5.338 Å | 105.098° | 930.2 Å ³ | 9.598 |
| A.26 ... | 9.962 | 18.201 | 5.343 | 105.177 | 934.9 | 9.614 |
| A.28 ... | 9.974 | 18.203 | 5.345 | 105.032 | 937.3 | 9.633 |
| A.30 ... | 9.928 | 18.157 | 5.373 | 105.193 | 927.6 | 9.580 |
| A.29 ... | 9.948 | 18.185 | 5.342 | 105.150 | 932.9 | 9.603 |
| A.21 ... | 9.948 | 18.246 | 5.345 | 104.991 | 937.2 | 9.609 |
| A.24 ... | 9.926 | 18.221 | 5.324 | 104.881 | 930.6 | 9.593 |
| A.22 ... | 9.921 | 18.220 | 5.331 | 104.889 | 930.2 | 9.588 |
| A.23 ... | 9.899 | 18.173 | 5.319 | 104.877 | 924.8 | 9.567 |
| A.25 ... | 9.923 | 18.180 | 5.319 | 104.150 | 930.5 | 9.622 |
| *A.17 ... | 9.921 | 18.200 | 5.324 | 104.870 | 929.0 | 9.622 |
| *A.18 ... | 9.937 | 18.240 | 5.336 | 104.918 | 934.6 | 9.588 |
| *A.19 ... | 9.948 | 18.254 | 5.331 | 104.800 | 935.8 | 9.603 |
| *A.20 ... | 9.948 | 18.251 | 5.344 | 104.895 | 937.8 | 9.618 |
| 5. ... | 9.933 | 18.058 | 5.309 | 104.15 | 918 | — |
| 6. ... | 9.882 | 18.080 | 5.322 | 105.32 | 917 | — |

* From M. T. Frost, 1963.

TABLE VI. Powder data for A.23. Values of *hkl*, $2\theta_0$, $2\theta_c$, $2\theta_0 - 2\theta_c$, $\sin^2\theta_0 - \sin^2\theta_c$, the drift constant and $(\delta)^2$, the estimated external standard deviation squared

| <i>hkl</i> | $2\theta_0$ | $2\theta_c$ | $2\theta_0 - 2\theta_c$ | $\sin^2\theta_0 - \sin^2\theta_c$ |
|--------------|-------------|-------------|-------------------------|-----------------------------------|
| 110 | 12.150° | 12.159° | -0.009° | -0.0000168 |
| 040 | 22.751 | 22.737 | 0.014 | 0.0000464 |
| 131 | 30.520 | 30.525 | -0.005 | -0.0000207 |
| 240 | 31.544 | 31.538 | 0.006 | 0.0000279 |
| 310 | 33.112 | 33.118 | -0.006 | -0.0000281 |
| 221 | 35.279 | 35.369 | 0.010 | 0.0000513 |
| 330 | 36.990 | 36.988 | 0.002 | 0.0000117 |
| 33 $\bar{1}$ | 37.970 | 37.970 | 0.000 | -0.0000017 |
| 151 | 38.379 | 38.386 | -0.007 | -0.0000401 |
| 06 $\bar{1}$ | 40.110 | 40.118 | -0.008 | -0.0000423 |
| 20 $\bar{2}$ | 41.030 | 41.027 | -0.003 | 0.0000147 |

Drift constant -5.07×10^{-4} , $(\delta)^2 = 1.8 \times 10^{-9}$.

parameters using observed 2θ values. A drift constant, with a trigonometrical function, $\cos^2\theta \cdot \sin\theta$, was determined with each set of parameters. The accuracy of the cell parameters were estimated from the reciprocal matrix of the normal equations and the estimated external standard deviation, and was found to be approximately $\pm 0.05\%$ of the computed value.

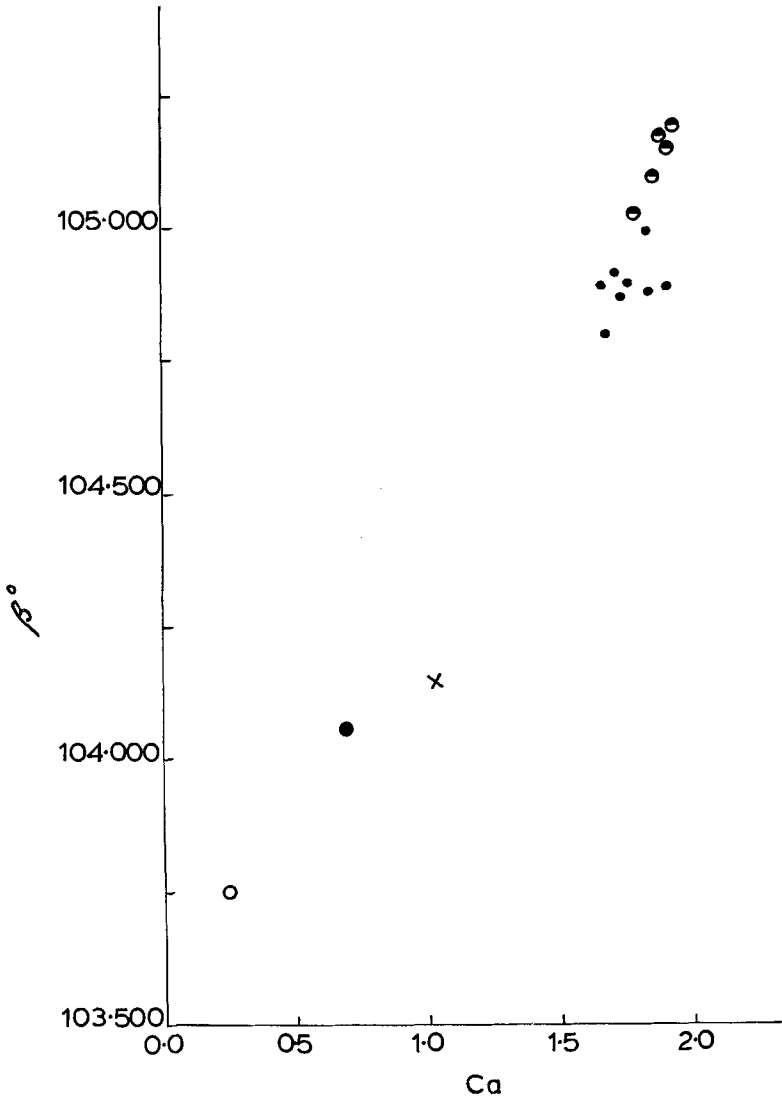


FIG. 5. Increase in β with increase in Ca content of amphiboles. ● Nigerian hastingsites; ○ Marangudzi hastingsites; X A. 25, intermediate amphibole; ● A. 16, Ca-rich arfvedsonite; ○ mean of 14 Nigerian arfvedsonites.

Results. The values of the cell parameters, $a \sin\beta$ and cell volume are tabulated in table V. As an illustration, the values of hkl , $2\theta_o$, $2\theta_o - 2\theta_c$, and $\sin^2\theta_o - \sin^2\theta_c$, the drift constant and the estimated external standard deviation for A.23 are shown in table VI.

Conclusions. Three general points emerge from the above data. The values of a , b , c , and $a \sin\beta$ are all large. The high values of b can be mainly attributed to the high content of total iron and Ca and those of $a \sin\beta$ to high total iron. The replacement of Si by Al^{III} and Fe^{III} probably accounts for the high values of c .

β increases with increasing Ca (see fig. 5). This supports Whittaker's (1960) conclusion that it is the nature of the ion in the X group that mainly determines the value of β . (Note that β [C2/m] increasing with increasing Ca is equivalent to β [I2/m] decreasing with increasing Ca; see Whittaker and Zussman, 1961). The fact that the Ca content of A.25 and its value of β (104.150°) are intermediate between the arfvedsonite and ferrohastingsite suggests that a continuous series does exist between the two subgroups.

Acknowledgements. The first author wishes to thank Dr. Carmichael of Imperial College for his advice during the course of the work and for critically reading the manuscript. Thanks are also due to Prof. J. Sutton for commenting on the manuscript, Dr. Howie of Manchester University for permission to publish two analyses of barkevikite, and to Drs. A. C. Gifford and G. Rees for separating and providing the samples of hastingsite from Marangudzi.

The second author wishes to thank Prof. W. A. Deer and the University of Manchester for providing the facilities for research, and is indebted to Dr. J. Zussman for his helpful advice and suggestions during the course of study.

Both authors acknowledge financial assistance from the D.S.I.R.

References

- BILLINGS (M. P.), 1928. *Amer. Min.*, vol. 13, p. 287.
 BORLEY (G. D.), 1963. *Min. Mag.*, vol. 33, p. 358.
 BUDDINGTON (A. F.) and LEONARD (B. F.), 1953. *Amer. Min.*, vol. 38, p. 891.
 CHINNER (G. A.), 1960. *Journ. Petrology*, vol. 1, no. 2.
 DEER (W.), HOWIE (R. A.), and ZUSSMAN (J.), 1963. *Rock Forming Minerals* (London), vol. 2.
 FROST (M. T.), 1963. *Min. Mag.*, vol. 33, p. 377.
 GIFFORD (A. C.), 1960. Unpublished thesis, University of London.
 HALL (A. J.), 1941. *Amer. Min.*, vol. 26, p. 29.
 HOWIE (R. A.), 1963. *Min. Mag.*, vol. 33, p. 718.
 JEFFERY (P. G.) and WILSON (A. D.), 1960. *The Analyst*, vol. 85, p. 478.
 REES (G.), 1960. Unpublished thesis, University of London.
 SUNDIUS (N.), 1946. *Årsbok Sverig. Geol. Undersok.*, vol. 40, no. 4.
 TRÖGER (W. E.), 1956. *Optische Bestimmung gesteinsbild. Min.*, 2nd edn., Stuttgart.
 WHITTAKER (E. J. W.), 1960. *Acta Cryst.*, vol. 13, p. 291.
 — and ZUSSMAN (J.), 1961. *Ibid.*, vol. 14, p. 54.
 WILKINSON (J. F. G.), 1961. *Amer. Min.*, vol. 46, p. 340.