

Amphiboles from the Younger Granites of Nigeria.
Part II. X-ray data.

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Summary. The cell parameters of fifteen arfvedsonites and four ferrohastingsites were determined using powder and diffractometer techniques and a least squares method of computation. Methods are proposed of distinguishing between calcium- and sodium-rich amphiboles, and between iron-rich and iron-poor varieties of these two groups, by their powder data. Within the arfvedsonite group the *b* parameter was found to increase with increasing Ca, Fe²⁺, and (OH) and to decrease with increasing Na, F, and Li. The *c* parameter was found to decrease with increasing F and increase with increasing (Fe³⁺ + Al + Ti). The parameters *a*, *β*, and *a sin β* all tended to increase with increasing Ca, Fe²⁺, and F content. The cell volumes were found to vary with the *b* parameter. The ferrohastingsites were found to have much larger cell parameters than the arfvedsonites. An attempt was made to explain these variations from structural considerations.

IN part I the petrography, optical properties, and chemical analyses of a number of amphiboles from the Younger Granites of Nigeria were described by Mrs. G. D. Borley.² Part II presents the results of a study of the same specimens using X-ray methods.

Experimental method.

Cell parameters were determined using a Philips X-ray diffractometer and Co-*K*_α radiation. At first the position of each reflection was estimated with respect to those from a quartz standard that had itself been checked by a silicon standard. It was, however, found more satisfactory to use no internal standard, with the advantage that the intensities of the reflections increased, and there was no contamination of the specimen. Instead a least squares solution was used, which included a drift constant to allow for non-random errors. Each specimen was well ground in an agate mortar and packed in a glass cavity approximately 5 × 10 mm in dimensions. Instrument settings were as follows: time constant 4; scanning speed 1°/min; chart speed 400 mm/h; divergence

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² See preceding paper, this vol., p. 358.

and scatter slits 1° ; chart measurements of 2θ were made up to about 50° in 2θ , in most cases on three separate traces. Between each trace the specimen was reground and remounted. These 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.

To investigate possibilities of unmixing, single-crystal photographs were taken using oscillation and Weissenberg cameras. No trace of this phenomenon has been found so far.

Computation.

The indexing of the reflections and the calculation of the cell constants were carried out with the aid of Manchester University's Mercury computer. An iterative least squares method was used that calculated shifts of $(a^*)^2$, $(b^*)^2$, $(c^*)^2$, $a^*c^* \cos \beta$, and K_0 , the drift constant, from their assumed approximate values. The variance and covariance of each term was calculated from the reciprocal matrix, Δ^{-1} , of the normal equations. Their standard errors were obtained from the expression:

$$(\text{S.E.})_p^2 = \Delta_{ii}^{-1} (\hat{\sigma})^2, \text{ where } \rho = (a^*)^2, (b^*)^2, (c^*)^2 \text{ or } a^*c^* \cos \beta,$$

and where Δ_{ii} is the i th term of the reciprocal matrix and $(\hat{\sigma})$ is the estimated external standard deviation obtained from the expression:

$$(\hat{\sigma})^2 = \sum_N w(\sin^2\theta_0 - \sin^2\theta_c)/(N - m),$$

w representing the weight of an observation, N being the number of observations, and m the number of parameters. The standard errors of the parameters were calculated from $(\hat{\sigma})$ and the variances and covariances of the terms refined and were found to be ± 0.006 , ± 0.010 , $\pm 0.003 \text{ \AA}$, and $\pm 0.05^\circ$ for a , b , c , and β respectively.

In an attempt to take into account major non-random errors Cohen (1936), and Hess (1951) used the relationship,

$$n^2\lambda^2/4d^2 = \sin^2\theta + K_0\psi_0,$$

where ψ_0 is a trigonometrical function appropriate to the experimental method. For the first iteration the drift constant K_0 was assumed zero and the value of K_0 first determined was not found to change significantly in any subsequent iteration. The best trigonometrical function was found to be $\sin \theta \cdot \cos^2\theta$. Several others were tried, including $\cos \theta$, $\cos^2\theta$, and $\sin^2 2\theta$, but none proved as satisfactory. It was found that with the introduction of this drift constant $\sum_N |2\theta_0 - 2\theta_c|$ always decreased.

Results.

Table I shows the cell parameters of the 15 Nigerian arfvedsonites (A.1 to A.16) and 4 ferrohastingsites. The space group $C2/m$ has been adopted in all cases. Table II shows, as an example, the indices, $2\theta_o$, $2\theta_c$, $2\theta_o - 2\theta_c$, and $\sin^2\theta_o - \sin^2\theta_c$ for specimen A.1.

TABLE I. The cell parameters of the arfvedsonites and ferrohastingsites. The $C2/m$ orientation has been used in all cases. Reference numbers as in part I. A.10 was not chemically analysed.

Reference number.	a (Å).	b (Å).	c (Å).	β (Å).	$a \sin \beta$ (Å).	V (Å ³).
A.1	9.810	17.943	5.307	103.83	9.525	907.0
A.2	9.865	18.066	5.326	103.79	9.581	921.9
A.3	9.841	18.036	5.318	103.74	9.560	922.0
A.4	9.839	18.087	5.334	103.78	9.556	921.9
A.5	9.806	18.047	5.329	103.71	9.527	916.2
A.6	9.824	18.061	5.332	103.77	9.542	918.9
A.7	9.847	18.009	5.313	103.73	9.564	915.1
A.8	9.824	18.006	5.320	103.74	9.542	914.0
A.9	9.837	18.033	5.321	103.68	9.558	917.1
A.10	9.824	17.988	5.319	103.80	9.540	912.8
A.12	9.825	17.995	5.321	103.79	9.542	913.7
A.13	9.830	18.015	5.319	103.71	9.550	915.1
A.14	9.813	17.954	5.310	103.66	9.535	909.0
A.15	9.837	18.014	5.321	103.71	9.557	916.1
A.16	9.898	18.128	5.319	104.01	9.602	925.8
A.17	9.921	18.200	5.326	104.87	9.588	929.4
A.18	9.933	18.213	5.332	104.92	9.599	932.2
A.19	9.947	18.271	5.331	104.80	9.628	937.8
A.20	9.949	18.251	5.344	104.90	9.614	937.7

TABLE II. Values of $2\theta_o$, $2\theta_c$, $2\theta_o - 2\theta_c$, $\sin^2\theta_o - \sin^2\theta_c$, and approximate relative intensity for each reflection used in the computation of the cell parameters of A.1. Drift constant $K_0: 7.9 \times 10^{-4}$.

hkl	$2\theta_o$.	$2\theta_c$.	$2\theta_o - 2\theta_c$.	$\sin^2\theta_o - \sin^2\theta_c$.	I .
110	12.172	12.160	0.011	0.000021	> 10
130	20.284	20.297	-0.013	-0.000024	2
040	22.978	22.959	0.019	0.000066	6
131	30.445	30.439	0.006	0.000028	7
240	31.758	31.751	0.007	0.000032	8
310	32.203	32.204	-0.001	-0.000004	> 10
330	37.154	37.155	-0.001	-0.000004	7
151	38.482	38.487	-0.007	-0.000035	9
061	40.418	40.421	-0.003	-0.000014	3
20 $\bar{2}$	41.300	41.301	-0.001	-0.000008	3
351	45.251	45.247	0.004	0.000028	2
261	48.730	48.727	0.003	0.000020	3

Comparison between amphibole sub-groups.

Arfvedsonite and other soda-amphiboles can be distinguished from Ca-amphiboles by their β values. Powder patterns show this clearly by the separation of the two reflections 151 and $33\bar{1}$. In arfvedsonite and riebeckite their 2θ values are almost identical, but with the increase of β their separation becomes progressively greater. The cummingtonite-grunerite series, where Fe^{2+} completely replaces Na and Ca, have much smaller values of β (102.1°). However, this series can be most easily distinguished by the 2θ value of the 310 reflection. The cummingtonite group have high 2θ values (about 34.2° 2θ Co- $K\alpha_1$, or a d value of 3.038 \AA), whereas the Na- and Ca-amphiboles have much lower values (about 33° 2θ Co- $K\alpha_1$, or a d value of 3.24 \AA). In each of these subgroups the b -axis decreases when Fe^{2+} is replaced by smaller ions such as Mg and Li. An estimate of b can be most easily obtained from the reflection 040. The b axis is considered large when 2θ is less than 22.90° Co- $K\alpha_1$ (a d value of 4.506 \AA) and small when 2θ is greater than this angle. The ferrohastingsites (see table I) have much larger b values (about 18.2 \AA) than the corresponding Ca-rich, Fe^{2+} -poor types such as tremolite, which has a b axis of about 18.05 \AA . The riebeckite-arfvedsonite group has b values of about 18.0 (a d value of about 4.49 \AA) whereas glaucophanes, in which Fe^{2+} and Fe^{3+} are replaced by Mg and Al respectively, have b parameters well below 18.0 \AA . As an example of the latter, the cell parameters of a glaucophane from Zermatt (obtained from Zurich University) were computed; this glaucophane has a 9.538 \AA , b 17.725 \AA , c 5.296 \AA , β 103.744° , giving a cell volume of 869.8 \AA^3 . From this general survey, therefore, it is evident that the value of β is an approximate guide to the type of atom in the X site, and that the size of the b dimension gives some estimate of the Fe^{2+} content within the Y site.

The Nigerian arfvedsonites and ferrohastingsites.

The b parameter: fig. 1 illustrates that for the Nigerian arfvedsonites the b parameter increases with increasing Ca and Fe^{2+} and decreases with increasing Na, F, and Li. This trend extends to the ferrohastingsites where Ca, Fe^{2+} , and (OH) are much higher, Li much lower, and b is often greater than 18.2 \AA . Fig. 2 illustrates that the two ions of the X group and two of the five ions of the Y group lie between, and link, the double amphibole chains and that the repeat distance along the b -axis is influenced by these links. From these considerations it seems probable that b increases when the size of the linking cations increases (i.e. when

Ca replaces Na, and Fe^{II} replaces smaller atoms such as Li), and decreases when the size of the chains themselves contracts. F is likely to contract the chains as it is more electronegative, and would thus hold more tightly the cations within the chains. The replacement of Si by the

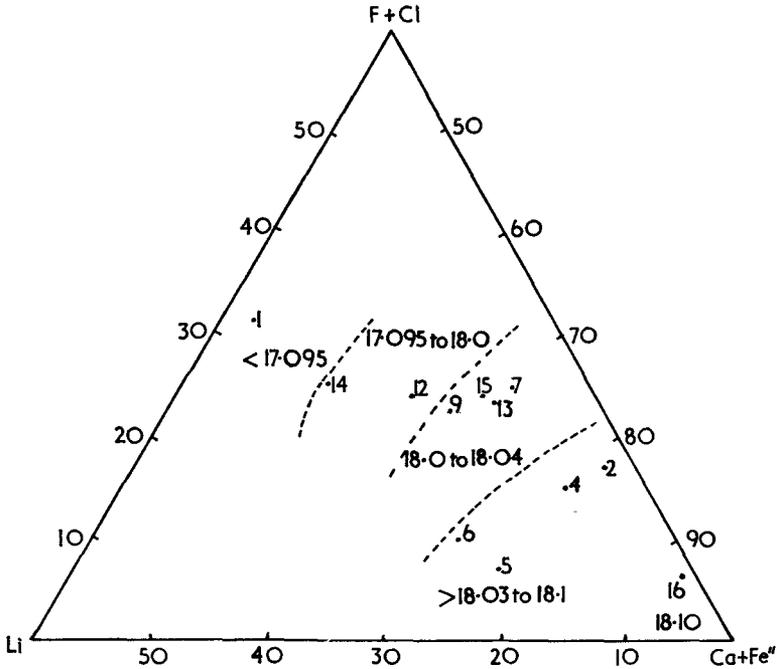


FIG. 1. A plot of (Ca+Fe^{II}), Li, and F (atoms %) of 14 Nigerian arfvedsonites. The reference number (see part I) is written beside each point. Dashed lines group the points into ranges of *b*, which increases with Fe^{II} and Ca and decreases with increasing F and Li. The cell volume varies in a similar manner.

slightly larger cations such as Fe^{III} and Al^{III} might increase *b* by increasing the size of the tetrahedra of the chains. However, the correlation between these types of ions and *b* is low, and probably the effect of this replacement on *b* is masked by the much greater effects of the variations of the cations within the X and Y sites.

The c parameter: as with *b*, decreasing values of *c* can be related to increasing values of F. The *c* parameter, unlike *b*, is not directly affected by the interchain bonds and it is probably because of this that *c* does not vary significantly with either Ca or Fe^{II}. However, it is related to the

small high valency cations; thus, as fig. 3 illustrates for the arfvedsonites, high values of c are observed when F is low and also when $(\text{Fe}^{III} + \text{Al} + \text{Ti})$ is high. The replacement of Si by such ions might increase the dimensions of the chains and thus would account for the

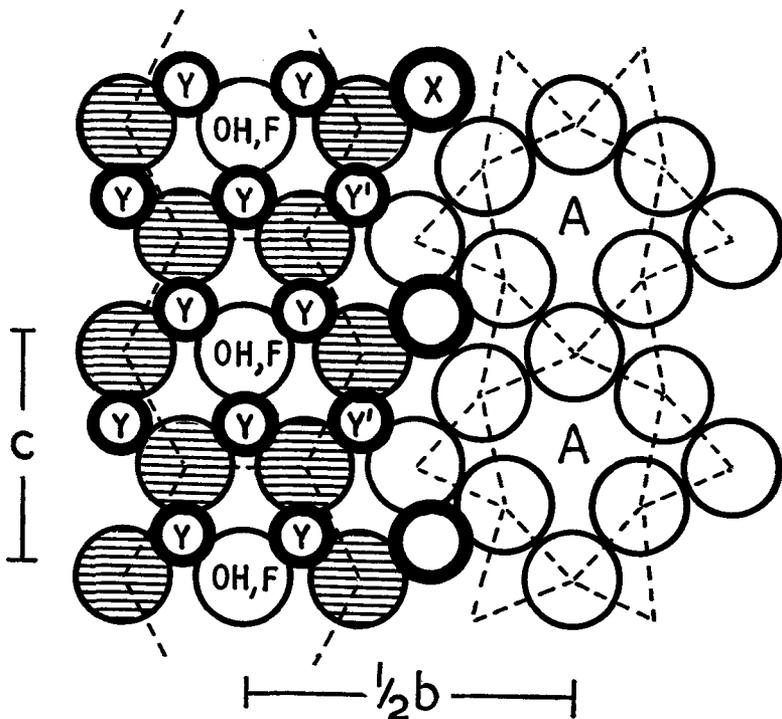


FIG. 2. Shows the general features of a monoclinic amphibole projected on to (100). Large circles (shaded or unshaded) represent oxygen atoms. Those shaded represent oxygens belonging to one chain and those not shaded to another, which is inverted with respect to the shaded chain. Cations marked Y' and X link the two chains whereas other Y atoms and the (OH, F) atoms have no interchain bonds. The A sites of the inverted chain are indicated.

increase in c . That Si is replaced by these cations seems probable as Si tends to decrease with increasing $(\text{Al}, \text{Fe}^{III}, \text{Ti})$. Moreover, the trend found in the natural arfvedsonites also occurs within the synthetic riebeckites and natural ferrohastingsites. Synthetic riebeckites have high values of c (about 5.33 \AA), moderate amounts of Fe^{III} , and no F . The ferrohastingsites also have high values of c (about 5.34 \AA), much replacement of Si by Al and very little F .

a, β , and cell volume: as with *b*, both *a* and β are related to Ca, Fe²⁺, and F content. High Ca, Fe²⁺, and (OH)⁻ usually accompany high values of *a*, β , and consequently *a* sin β . Again these trends are found to extend to the ferrohastingsites where *a*, *a* sin β , and β are all much larger. The correlation between composition and these parameters is lower than in the case of *b* and *c*. There are anomalies such as specimen A.1, which

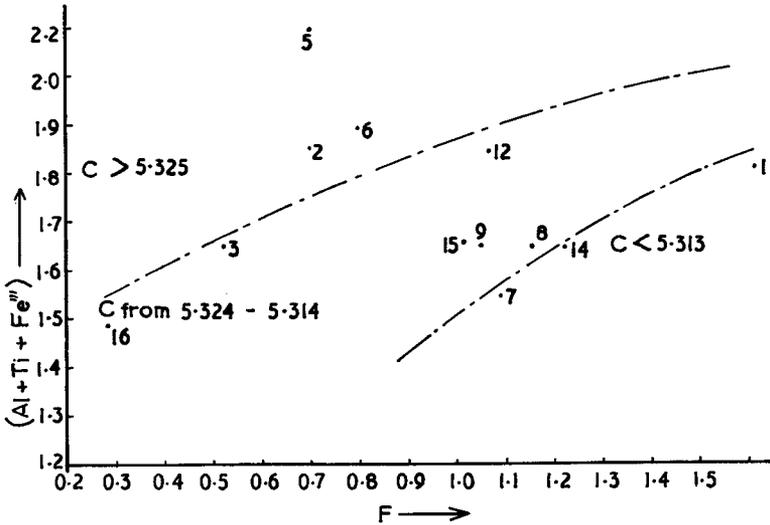


FIG. 3. A plot of the amount of (Al + Fe²⁺ + Ti) against F (atoms per half unit-cell) of the Nigerian arfvedsonites. Reference numbers (see part I) are given beside each point. The diagram shows how *c* increases with increasing (Al + Fe³⁺ + Ti) and decreasing F.

has a high β , but low Ca and (OH). As all parameters tend to increase with similar variations in chemistry, the cell volumes also increase with these variations. The variation is very similar to that of the *b* parameter (see fig. 1), i.e. volume increases with Fe²⁺, Ca and (OH), and decreases with increasing Li and F.

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